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**Results of a Workshop Meeting to Discuss Protection of  
Public Health and Safety During Reentry into Areas  
Potentially Contaminated with a Lethal Chemical  
Agent (GB, VX, or Mustard Agent)**

**Background**

As a result of recent laws, the United States' stockpiles of lethal chemical weapons will be destroyed. Destruction will be by incineration at the eight facilities where the stockpiles are kept. Although there is only a remote chance of a release of any chemical agent, either from the storage facilities or from an incineration plant, we are developing plans to manage that eventuality.

These comments are provided for consideration by Army and Federal Emergency Management Agency (FEMA) planners who are preparing a series of emergency response guidance papers to assist local and State civil authorities and Army planners following an unplanned release of a lethal chemical agent (GB; VX; or mustard agents: H, HD, HT). Other parts of the series deal with evacuation and additional measures to protect people in the immediate aftermath of a release; this portion deals only with a later phase, when citizens return home.

An interagency steering committee, cochaired by the Army and FEMA, worked for several months to prepare guidelines. Oak Ridge National Laboratory staff, under contract to the Army, prepared a manual, "Reentry Planning: The Technical Basis for Offsite Recovery Following Warfare Agent Contamination" (ORNL-6628; Oak Ridge National Laboratory, Oak Ridge, TN 37831-6101). On March 5 and 6, 1990, the Centers for Disease Control hosted a workshop for a group of scientists and public officials to discuss issues related to reentry. In addition to the participants in the workshop, a number of other guests attended and contributed to the deliberations. The participants are listed in Appendix A. A transcript of the meeting is available on request from the Special Programs Group, Center for Environmental Health and Injury Control, 1600 Clifton Road NE, (F29), Atlanta, Georgia 30333.

**Introduction**

These suggestions are intended to protect the most sensitive members of the population--infants and people with severe respiratory impairment. Other special groups, such as pregnant women or the aged, may be more vulnerable to the effects of agents than the general population, but they probably would not be more affected than infants and those with severe respiratory disease. This paper provides interim guidance based on information now available and identifies areas where more information or further research is needed before final reentry standards can be established.

Reentry planning must be done before the onset of an emergency and reentry and recovery efforts must begin during the response phase of an emergency. If work on reentry is delayed until after the response to the initial emergency has been completed, both time and critical information will be lost, and damage to livestock, in particular, may be greatly and unnecessarily increased.

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HHS, PHS, CDC

Mobilization of State and national experts as soon as possible after such an event is critical; they must modify these recommendations to deal effectively with the specifics of the situation as it develops. Although an Army on-scene commander will carry out the functions of the Federal on-scene coordinator, the governor of a State has the responsibility and authority for protecting civilians. Various State agencies, the county sheriff, and county and municipal authorities share additional responsibilities and authority. Most of the actions considered here also are regulated under Federal laws dealing with spills of hazardous materials and cleanup of contaminated sites. Because of the unique properties of the lethal chemical agents, the resources to respond to a catastrophic release must come largely from the Army or other Federal agencies. All consultants must remain aware that their role is to work in a unified command structure, aiding and advising State, county, and municipal authorities as well as the on-scene commander.

To this end, planners must identify by name those individuals in the State with special knowledge likely to be helpful in an emergency; confirm in advance those persons' willingness to assist in an emergency; and maintain a well-indexed inventory of the skills available so that advisory teams can be assembled quickly. Examples might include veterinarians, soil scientists, laboratory personnel, sanitarians, agricultural extension workers, Army retirees with special skills, and medical personnel with knowledge of chemical agents. Planners must include State and local personnel in both sampling and analytical procedures; under the circumstances contemplated here, the public will want State and local assurance that all environmental testing is done correctly.

We believe these suggestions will remain adequate for an incident involving GB. With VX and mustard, the hazard resulting from slow desorption of agent from droplets falling on porous surfaces is a particularly difficult problem, however. Whether the hazard persists depends on the temperature (mustard and VX will evaporate from surfaces more quickly in hot weather); rainfall and humidity (mustard and VX will be washed off surfaces by rain and will degrade into nontoxic chemicals more quickly in a humid environment); and the characteristics of the contaminated material. The interim nature of these suggestions is especially evident with respect to VX and mustard.

Contamination following a release will be local; that is, a limited area will be affected. Deposition of the agent will be uneven within the affected area; "hot spots" may have concentrations 10 or more times greater than surrounding "cold spots." Evaporation of mustard from the hot spots with redeposition onto less affected areas might create a problem. For that reason, sampling of areas, not just homes, will be required.

Some words of caution are in order. Because we believe that on-the-scene decisions by a team of experts will be especially important in ensuring public health and safety, these are to be read only as guidance; they are comprehensive but are not a complete set of directions to be followed rigidly. They must be integrated with other parts of the emergency response guidance series.

## **I. Information Gaps**

The workshop group that met in Atlanta in March 1990 identified the following areas where more information or research is needed to set final standards for reentry:

### **A. Analytical Methods**

We now have adequate methods to sample for all agents in air. Bench analysis of agents in water is now possible at 2 ng/ml (2 ug/l); planners need confirming documentation, however. Analytical methods for agents in various other substrates need to be developed or documented. Analysis of agents in soil would be accomplished by extraction; more information about recovery of agents adsorbed onto soil types that might be found near storage depots is needed. Sensitivity of detection of agents in several representative food stuffs should be demonstrated or documented (cf. 40 CFR 180.34f). Planners also need to know at what concentrations mustard agent can be detected in hair, hide, and feathers.

Workshop participants suggested studying the feasibility of developing an enzyme-linked immunosorbent assay (ELISA) to test for these lethal agents.

### **B. Indicator Compounds**

In some cases, metabolites or hydrolysis products are more persistent than the original toxicant; indicator compounds that may provide information about the degree of contamination should be identified, and the appropriate analytical capability should be made available.

### **C. Environmental Data**

Base line information to characterize the environment near the eight storage sites is needed. For the entire area at each site where deposition of agents could occur, soil and groundwater flow characteristics should be determined and land use data and detailed information on building locations should be collected. Soil in the area should be sampled to determine base line concentrations of agents, characteristic metabolites of agents, and other chemicals that would interfere with measurement of newly released agents. Survey sampling should be linked to the sampling plan for response to releases (see Section II, Subsection A).

### **D. Sentinel Species**

Sentinel species may be useful for several purposes. Immediately after a release, a survey of the area potentially affected may show depletion of insects, ground-dwelling animals, or birds. Evidence of such deaths would confirm passage of a significant plume.

Measurement of cholinesterase activity in domestic or wild animals at each site may show, with greater sensitivity, whether a low-concentration plume of nerve agent has passed. National planners should standardize the cholinesterase analytical method. Local planners must identify laboratories

capable of performing the requisite type and number of tests. Base line data on cholinesterase activity for selected species should be compiled at each site.

Responders may want to introduce species known to be sensitive to the effects of the agent, and then closely observe these animals to provide a convincing supplement to analytical measurements of agent concentration. Rabbits, small birds (chicks, canaries, or parakeets), pigeons, and featherless chickens have been suggested; chicks are probably most readily available throughout the year in the quantities that might be needed. Featherless chickens have been used in studies of occupational exposures to industrial chemicals. If blood samples are required to determine cholinesterase activity, keep in mind that larger animals are easier to bleed. Information on the sensitivity of various other animal species to the effects of both nerve agents and vesicants is also needed.

#### **E. Toxicity Data**

Data is needed to determine, with each agent, the levels of dermal and of oral exposure at which no adverse effect can be detected--the no-observed-adverse-effect level or NOAEL. These NOAELs can then be used to establish protective maximum permissible exposure levels by route of exposure. These levels must in turn be combined with information on dermal transfer coefficients in order to establish permissible residue levels on plants and other surfaces. Information on pesticide transfer coefficients for indoor surfaces and human activities (such as harvesting, animal management, and sleeping on contaminated ground) is now being developed for the U.S. Environmental Protection Agency.

#### **F. Adsorption/Desorption of Agents from Various Surfaces**

As stated, adsorption of the persistent agents onto porous surfaces may present a particularly difficult problem. Some materials bind agents so tightly that desorption would not be a significant health hazard. Information on the effect of paints or other coatings on desorption from various surfaces might also be useful.

#### **G. Other Considerations**

Adequate site-specific models for dispersion of agents in air and water are needed. Air dispersion models are presently available but may be improved. Water dispersion models are not available at installations.



## II. Suggested Interim Guidance

Actions to be taken during the period immediately after a release are listed first, followed by actions that would occur later in the recovery phase. Even though the sections on decontamination and on sampling analytical methods are presented last, they could be relevant to efforts at all phases of recovery.

### A. Time of exclusion

#### 1. General Approach

If no evidence were available to confirm safety, civil authorities would need to designate a very long minimum time before any persons not wearing protective masks and clothing could be allowed to enter a contaminated zone. Initial estimates indicate that minimum times would range from 48 hours for GB to 14 days for VX and mustard, whereas maximum times could be up to 2 weeks for GB and 90 days for VX and mustard. Because of the uncertainty in estimating the time requirements for any decontamination, sole reliance on a reentry interval for protection would unnecessarily delay resumption of normal activities and property use. Instead, we recommend establishing an initial quarantine (no-entry) period during which sampling and analysis of air, water, soil, and selected surfaces will be carried out to determine whether contamination exists. If no contamination is found, evacuees should be permitted to reenter in a phased manner, beginning with the areas least likely to have been contaminated. If contamination is encountered, decontamination must be completed and extensive environmental sampling in the area conducted before reentry may be considered.

#### 2. Implementation

Local planners and the Army should cooperatively develop generalized sampling strategies now, so that if an incident occurred, they could quickly develop plans specific to any actual release. Strategies should encompass sample control and laboratory procedures. Workshop participants suggested that a mobile laboratory, moved to the site of an emergency, might enhance the speed of testing.

If a release results in a hazard beyond the installation boundary, responders would need to spend several days assembling the necessary personnel and equipment and conducting the surveys needed to assure evacuees that they may safely return. The time required to test and certify safety will vary with the area affected. For the simplest case, a release of GB, a minimum wait of 3 days should be anticipated before the first potentially affected area could be certified safe and a minimum wait of 5 days should be anticipated before all potentially affected areas could be certified safe. Actual times might be much longer, depending on the agent and circumstances of the release.

### B. Personal Property

Articles removed from a contaminated area must be certified agent-free or be disposed of in an environmentally sound manner. Articles in evacuated areas that were not reached by an agent plume will not require any testing;

however, as laboratory staffs complete more urgent work, they may need to provide such testing on request, to restore public confidence and peace of mind.

#### C. Human Remains

A release with off-site consequences could cause deaths among civilians. If fatalities occur from any cause, the site should not be disturbed nor bodies moved until a proper coroner's investigation has been conducted and the remains have, if necessary, been decontaminated. Surface decontamination should be sufficient if the agent is GB; for other agents, closed-casket burial may be prudent. For further details, refer to "Reentry Planning" (ORNL, op. cit.).

#### D. Care of Livestock and Property Before Return is Safe

Between the time of release and the time when the conditions specified in Sections G or H are met, Army and/or local personnel in protective clothing will provide necessary feeding and care for animals and will perform other essential functions. If too few people are available to perform these tasks, priorities must be set: first, to protect human life and health; second, to minimize damage to livestock and companion animals; third, to protect other property; fourth, to protect crop plants.

As part of your emergency planning, the composition and responsibilities of caretaker teams should be identified now, before a release occurs. Planners should draw upon the experience and expertise of local veterinarians, agricultural extension staff, livestock managers, and members of animal husbandry and humane societies. Responders must know and maintain records of the location of both animals and their water and feed sources and of emergency feed supplies. They must obtain permission from the owners to enter for this purpose before a release, because people often go to friends' or relatives' homes in an evacuation and are difficult to locate.

#### E. Food and Water for Livestock

Food for livestock should be selected from lots stored in protected areas (silos, barns, bins, bags) and under protective layers (plastic, bales, discordable feed). As testing of food becomes available, animal fodder should be restricted to material containing agent concentrations less than those given in Table 1.

Table 1

Agent	Maximum Concentrations in micrograms per kilogram (ug/kg) of Agent in Animal Food
GB, VX	0.1
mustard	0.00 at analytical sensitivity of 0.01 ug/kg or less

Emergency management planners, should determine how they could provide large amounts of water for both drinking and contamination reduction purposes. They should plan to drain and refill stock tanks where ground water supplies are the source. Under the conditions envisioned, the water will not add significantly to general environmental contamination and may be allowed to run out to the ground. In areas where surface water is used, water safety must be tested as rapidly as possible. Expedient measures, such as addition of lime and hypochlorite to stored water, that can be taken when testing or alternate water supplies are unavailable should be considered.

#### F. Dairy Products

Nerve agents are not known to be secreted in milk, even in severely exposed animals. No extraordinary treatment of milk drawn from asymptomatic animals is necessary to protect human health. Nevertheless, to assure public peace of mind, dairy products from animals in a potentially affected area should be discarded for 72 hours after the animals are first known to be asymptomatic. Because the products will not be contaminated with agent (and could actually be consumed in an emergency), they may be disposed of in any manner which does not itself create a public health or environmental problem.

Antidotes to nerve agents (atropine or 2-PAM Cl) can, however, contaminate dairy products. If these antidotes have been used, the Food and Drug Administration (FDA) or appropriate State authority must determine acceptable antidote residue levels or direct the disposition of products.

If, on the basis of modeling or other information, dairy animals are believed to have been exposed to mustard agent at concentrations greater than the 8-hour time-weighted average for human workers, they should be used only for breeding stock or they should be destroyed and disposed of in a humane and environmentally sound manner.

If dairy animals have been exposed to mustard agent at concentrations less than the 8-hour time-weighted average for human workers, the milk should be tested for presence of mustard agent and mustard hydrolyzates, using the best analytical methods available. The methods should be approved by the FDA and appropriate State authorities. Discard dairy products with elevated concentrations of mustard hydrolyzates in an environmentally sound manner. No doubt that dairy products with detectable amounts of mustard agent would be encountered following a release; if they should be, they must be held for disposal by the Army.

**G. Restricted Return to Potentially Contaminated Areas**

1. Civilians may return to evacuated areas, provided all of the following conditions have been met:
  - a. The governor or other appropriate civil authority has determined that no liquid agent reached the area to be visited, or authorized survey teams have verified by sampling and analysis that no liquid or absorbed surface contamination exists in the areas to be visited. (Technical advice to the civil authority and testing must be provided by the Army. Oversight of all phases by employees of State or local governments will enhance acceptance of the process by the general public.)
  - b. Sampling in the buildings and areas to be visited has shown that airborne concentrations of agents do not exceed the 8-hour time-weighted average for permissible workplace exposure to agents (see Table 2).
  - c. Sampling in the buildings was done with ventilation and temperatures representative of the ambient working conditions expected during the visit.
  - d. The people returning were not clinically affected by the original agent release, as determined by history of location well outside the plume area during the release or absence of symptoms combined with normal blood cholinesterase activity if a nerve agent is involved.
  - e. The risk of new releases of agents that might be life-threatening to the people entering is deemed to be negligible.
2. Once these conditions are met, people may return:
  - a. for possessions, to care for animals or property, or for other urgent purposes;
  - b. for periods not to exceed 8 hours in any 24-hour period;
  - c. after registration with proper civil authorities;
  - d. in pairs or groups of three.

Table 2

Maximum permissible concentrations (mg/m<sup>3</sup>)  
of airborne agents for occupational exposure and for  
continuous general population exposure

Agent	Occupational Exposure <sup>1</sup>	General Population Exposure <sup>2</sup>
GB	$1 \times 10^{-4}$	$3 \times 10^{-6}$
VX	$1 \times 10^{-5}$	$3 \times 10^{-6}$
mustard	$3 \times 10^{-3}$	$1 \times 10^{-4}$

<sup>1</sup> 8-hour time-weighted average

<sup>2</sup> 72-hour time-weighted average

**H. Return for Permanent, Unrestricted Use**

People may return for permanent, unrestricted use, provided these conditions have been met:

1. The governor or other appropriate civil authority has certified that no liquid agent reached the area to be visited, or authorized survey teams have verified by sampling and analysis that no liquid or absorbed surface contamination exists in the areas to be occupied.
2. Sampling in the buildings and areas to be occupied has shown that airborne concentrations of agents do not exceed the levels permitted for general population exposure.
3. Sampling in buildings was done under the worst probable case conditions—that is, with the building as warm as it is expected to become and with minimal air exchange between indoor and outdoor air.
4. The risk of new releases of agents is deemed to be no greater than before the event that triggered evacuation.

**I. Crops**

Any growing crops thought, on the basis of modeling or other information, to have been exposed to mustard agent at concentrations greater than the 8-hour time-weighted average for human workers should not be harvested for use as human food. Any crops believed to have been exposed to nerve agent at concentrations greater than the 8-hour time-weighted average for human workers should be destroyed (plowed under or otherwise disposed of in an environmentally sound manner) or, provided they fall below the maximum concentrations given in Table 1, they may be used for animal fodder. Any crops exposed to mustard agent should be sampled for the presence of mustard and, if the results warrant, disposed of in an environmentally sound manner. If mustard agent is found in or on the crops, the crops should be let stand for 1 year before the land is used. Retesting should be done near the end of that period; the quarantine could then be lifted under most conditions, and the crops could be plowed under or, if necessary, they could safely be removed for disposition elsewhere. Burning standing crops entails a risk of volatilization and spread of agents if contamination is heavy.

**J. Water Purity**

Water may be used without restrictions, provided these conditions have been met:

1. Drinking water is the only potential route of exposure.
2. The water contains no other toxic material.
3. Residues of agent are less than the concentrations given in Table 3.

If water supplies fail to meet these standards, alternate water supplies must be provided for all purposes.

Table 3  
Recommended Maximum Concentration  
Limits for Agents in Water

<u>Agent</u>	<u>Concentration</u>
GB, VX	0.14 ng/ml
HD	0.40 ng/ml

#### K. Stored Foods

If stored foods are known to have been exposed to agent liquid or to agent vapors in concentrations greater than the 8-hour time-weighted average approved for occupational exposure, they should be disposed of in an environmentally safe manner. Canned foods may be used after appropriate surface decontamination or may, at the discretion of appropriate authorities, be consumed.

#### L. Animal Carcasses

Livestock killed by agent exposure should be disposed of in an environmentally safe manner. If environmental regulatory authorities approve, they may be buried with hypochlorite and alkali to provide a measure of decontamination for any agent that may be on the animal's hide, fur, or feathers. In general, livestock severely injured by exposure to mustard agent should be destroyed in a humane manner and the carcasses should be disposed of in an environmentally safe manner. Other livestock should be tested for contamination of fur or feathers; if agent-free, the animals may be used without restriction. For treatment and decontamination guidelines, refer to "Reentry Planning" (ORNL, op. cit.). Wild animal carcasses are likely to be dispersed and therefore to pose a minimal hazard to health at any single point; if large animal carcasses are encountered, they may be disposed of in the same manner as for domestic livestock.

#### M. Decontamination

If significant contamination is detected at any location, some or all of the following steps should be taken:

1. The area should be strictly quarantined.
2. Specialized Army teams should decontaminate, package, and remove any material with gross liquid contamination; the Army will manage ultimate disposal. Owners should be advised that decontamination will probably destroy the contaminated object. Structures and other immovable objects must be dealt with on a case-by-case basis.

3. As quickly as possible, surfaces should be rinsed with water or a decontamination solution that will not itself cause significant environmental damage. External building surfaces should be hosed using fire equipment. Alkaline solutions are more effective than neutral or acid solutions, and hypochlorite solutions are most effective for VX and mustard. Adding lime or another alkalizing material or hypochlorite to the decontamination water may be useful but must be weighed against the environmental damage that might result from the additive. Runoff from such operations will not, in general, contribute significantly to existing environmental pollution with agents and, in the interest of rapid response, need not be contained. (Additional information on this and related issues may be found in the Department of Army pamphlet 50-XX, Chemical Accident or Incident Response and Assistance (CAIRA) Operations, which is now in preparation. Appendix L is titled "Decontamination of Specific Items.")
4. With technical advisors, responders should determine further decontamination and testing requirements at the time of the event. The decisions will depend on the agent of concern, weather conditions, and available resources.
5. Contaminated earth may, if the volume is small, be packaged by specialized Army crews and removed to Army control for eventual incineration. Larger areas will probably have to be decontaminated by weathering, which may require a prolonged and strictly enforced quarantine.
6. Because mustard is a carcinogen, fabrics and other replaceable porous materials known or likely to have been contaminated with mustard should be removed and disposed of in an environmentally sound manner. This measure, combined with monitoring, will reduce risk to a level substantially lower than that generally recognized as safe.
7. Fabrics and other replaceable porous materials that are known or likely to have been contaminated with VX in the event that a catastrophic release occurs before adequate sampling methods have been developed should be similarly disposed of.
8. Local, State, and Federal authorities should agree on what additional corrective action is needed. The National Response Plan and regulations promulgated under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) must be observed.
9. Observations on sensitive species (possibly including insects) should be used to monitor the progress of decontamination. We emphasize that this suggests, but does not replace, laboratory analysis of environmental samples.

**N. Analytical Sensitivity and Quality**

During reentry, the analytical methods used to monitor agent concentrations to ensure the safety of personnel should have the following documented characteristics:

**1. Qualitative detection limits**

- a. Agent concentrations at one-half  $Z$  (where  $Z$  is the action level or no-observed-adverse-effect residue concentration) must be detected and the identity confirmed with a false negative rate of less than 5%.
- b. For agent concentrations above one-half  $Z$  but less than  $Z$ , the false negative rate should decrease by approximately 1% for each one-tenth  $Z$  increase in concentration.
- c. For agent concentrations greater than  $Z$ , the false negative rate should be less than 1%.

**2. Quantitative detection limits:**

- a. The sum of the analytical percent bias plus 2 times the analytical coefficient of variation for the method should be less than or equal to 35% for the concentration range of one-half  $Z$  to twice  $Z$ .
- b. For concentrations greater than twice  $Z$ , the sum of the two analytical elements may increase to no more than 50%.



**Appendix A  
Workshop Participants  
(Alphabetic by Last Name)**

The Workshop was monitored by Vernon N. Houk, M.D., Assistant Surgeon General, USPHS, Director, Center for Environmental Health and Injury Control (CEHIC), Centers for Disease Control (CDC) and moderated by Sanford S. Leffingwell, M.D.; M.P.H., Medical Director, USPHS, CEHIC, CDC.

Mark Basbor, Ph.D., Associate Director for Federal Facilities, Agency for Toxic Substances and Disease Registry (ATSDR), FHS.

Thomas J. Buodi, V.M.D., Pathology Associates, Inc., National Center for Toxicology Research (Designated Representative of the Food and Drug Administration, FHS).

Mr. Jack Dubose, Deputy Director, State of Arkansas Office of Emergency Services.

Mr. Phil Errico, Dietary Exposure Branch, Hazard Evaluation Division, Office of Pesticides, U.S. Environmental Protection Agency (EPA).

Mr. Denzel Fisher, Emergency Management Specialist, Technological Hazards Division, Federal Emergency Management Agency.

Robert Forney, Ph.D., Distinguished Professor Emeritus of Toxicology, Indiana University.

Mr. E. Kent Gray, Chief, CDC/ATSDR Emergency Response Group, FHS.

Gordon Goff, Captain, USPHS, Emergency Response Division, EPA.

Wayland J. Hayes, M.D., Ph.D., Professor Emeritus of Toxicology and Pharmacology, Vanderbilt University

Mr. Thomas Hess, Environmental Liaison Officer, Office of the Assistant Secretary of the Army (Installations, Logistics, and Environment).

Roger McIntosh, M.D., Major, MC, USA, Office of the Surgeon General of the Army

Mark McClanahan, Ph.D., Toxicologist, CEHIC, FHS, CDC.

Donald Morgan, M.D., Ph.D., Professor Emeritus, Department of Preventive Medicine: Environmental Health, University of Iowa College of Medicine.

Richard M. Perry Jr., Ph.D., Deputy Assistant Administrator, Office of Cooperative Interactions, Beltsville Agricultural Research Center, U.S. Department of Agriculture

Mrs. Elisabeth Peterson, Physical Scientist, Headquarters, U.S. Army Armament Munitions and Chemical Command.

Elden P. Savage, Ph.D., Professor of Environmental Science, College of Veterinary Medicine and Biomedical Sciences, Colorado State University

James D. Adams, Ph.D., Non-Dietary Exposure Branch, Hazard Evaluations Division, Office of Pesticides, EPA.  
Nancy B. Minto, Ph.D., Health and Safety Research Division, Oak Ridge National Laboratory  
Annetta P. Watson, Ph.D., Health and Safety Research Division, Oak Ridge National Laboratory  
Paul Wojciachowski, Major, USA, Environmental and Monitoring Division, Office of the Program Manager for Chemical Demilitarization.

#### Other Guests

Mrs. Linda W. Anderson, Chief, Special Programs Group, CEHC, CDC.  
Mr. Charles Baronian, Technical Director and Deputy Program Manager for Chemical Demilitarization.  
Dennis Brown, Captain, USA, Army Environmental Hygiene Agency.  
Mr. Ronald C. Burger, CDC/NIOSH Emergency Response Group, PHS.  
Mr. Barry Davis, P.E., Special Programs Group, CEHC, CDC, PHS.  
Mr. Timothy P. Dowd, Region 4, FEMA.  
Caroline L. Harzenberg, Ph.D., Argonne National Laboratory  
Mr. Stephen L. Kistner, P.E., U.S. Army Environmental Hygiene Agency.  
Mr. Craig Pettani, Region 3, FEMA.  
Mr. James Rabb, CDC/NIOSH Emergency Response Group, PHS.  
John H. Sorenson, Ph.D., Oak Ridge National Laboratory.  
Richard J. Ward, Ph.D., U.S. Army Chemical Research and Development Engineering Center.  
Mr. Rurt Zimmerman, Environmental Health Administration, Utah Department of Health.

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**National Clearinghouse for Alcohol and Drug Information (NCADI)** P.O. Box 2845, Rockville, MD 20852, (301) 444-3800.

For additional information regarding the program and/or application procedures, contact:

**Division of Demonstrations and Evaluation, Office for Substance Abuse Prevention, ADAMHA,** Rockwall II Building, 9th Floor, 8600 Fishers Lane, Rockville, MD 20857, (301) 443-4364

or

**Office of Maternal and Child Health, HRSA, Parklawn Building, Room 6-37, 8600 Fishers Lane, Rockville, MD 20857, (301) 443-3730**

**Demonstration Grants for the Prevention, Treatment, and Rehabilitation of Drug and Alcohol Abuse Among High Risk Youth**

Under the authority of Section 505A of the Public Health Service Act, OSAP will accept applications from public and nonprofit private entities for projects to demonstrate effective models for the prevention, treatment, and rehabilitation of drug abuse and alcohol abuse among high risk youth. Proposals to demonstrate effective comprehensive service systems, particularly model service systems directed at primary prevention and early intervention, are a priority focus of this announcement. Approximately \$4 million will be available to support approximately 15-20 grants at an average award amount of \$200,000. The Catalog of Federal Domestic Assistance number for this program is 11.144.

Application kits including a copy of the complete Request for Applications and guidance for submission are available from: National Clearinghouse for Alcohol and Drug Information (NCADI), P.O. Box 2845, Rockville, MD 20852, (301) 444-3800.

For additional information regarding the program and/or application procedures, contact: Division of Demonstrations and Evaluation, Office for Substance Abuse Prevention, ADAMHA, Rockwall II Building, 9th Floor, 8600 Fishers Lane, Rockville, MD 20857, (301) 443-0336.

**Joseph S. Leone,**

**Associate Administrator for Management, Alcohol, Drug Abuse, and Mental Health Administration.**

(FR Doc. 98-18340 Filed 7-13-98, 8:45 am)

BILLING CODE 4160-10-0

## Centers for Disease Control

(Announcement No. 040)

**National Institute for Occupational Safety and Health, Farm Family Health and Hazard Surveillance Cooperative Agreement Program; Correction**

A notice announcing the availability of Fiscal Year 1990 funds for cooperative agreements to conduct population-based farm family health and hazard studies was published in the Federal Register on Wednesday, June 13, 1992, (57 FR 23622). The notice is corrected as follows:

On page 23624, third column, the information regarding the telephone number at the end of the first paragraph under the heading "Where To Obtain Additional Information," is corrected as follows: The telephone number is corrected from (404) 842-1830 and FTS 236-1830 to (404) 842-6530 and FTS 236-6530.

All other information and requirements in the notice remain the same.

Dated: July 8, 1998

**J. Brian Dupay,**

**Acting Director, National Institute for Occupational Safety and Health, Centers for Disease Control.**

(FR Doc. 98-18482 Filed 7-13-98, 8:45 am)

BILLING CODE 4160-10-0

## Technical Advisory Committee for Diabetes Translation and Community Control Programs; Meeting

In accordance with section 10(a)(2) of the Federal Advisory Committee Act (Pub. L. 92-463), the Centers for Disease Control (CDC) announces the following committee meeting.

**Name:** Technical Advisory Committee for Diabetes Translation and Community Control Programs.

**Time and Date:** 8 a.m. - 4:30 p.m., Monday, August 20, 1998.

**Place:** Lenox Inn, 335 Lenox Road, NE, Atlanta, Georgia 30326.

**Status:** Open to the public, limited only by the space available.

**Purpose:** This committee is charged with advising the Director, CDC, regarding priorities and feasible goals for translation activities and community control programs designed to reduce morbidity and mortality from diabetes and its complications. The Committee advises regarding policies, strategies, goals and objectives and prioritizes diabetes research advances and technologies ready for translation into widespread community practice; recommends public health strategies to be implemented through community interventions; advises on operational research and outcome evaluation methodologies; identifies research issues for further clinical investigation; and advises regarding the coordination of programs with

Federal, voluntary, and private agencies involved in the provision of services to people with diabetes.

**Matters to be Discussed:** The Committee will discuss scientific findings and mechanisms and the transfer of these findings into practice. Updates on major projects and activities currently underway within the Division of Diabetes Translation (DDT) will be presented. Events and recommendations from the American Diabetes Association's 80th Annual Conference will be summarized.

Agenda items are subject to change at priorities dictate.

**Contact Person for More Information:** Frederick C. Murphy, Program Analyst, DDT, Center for Chronic Disease Prevention and Health Promotion, CDC, 1600 Clifton Road, NE, Atlanta, Georgia 30333, telephone 404/639-1772, FTS 236-1772.

Dated: July 8, 1998.

**Diria Wilber,**

**Associate Director for Public Communication, Centers for Disease Control.**

(FR Doc. 98-18304 Filed 7-13-98, 8:45 am)

BILLING CODE 4160-10-0

**Availability of Document and Request for Comments on "Results of a Workshop Meeting to Discuss Protection of Public Health and Safety During Reentry into Areas Potentially Contaminated With a Lethal Chemical Agent (GB, VX, or Mustard Agent)"**

**Agency:** Centers for Disease Control (CDC), Public Health Service, HHS.

**Action:** Announcement of Availability and Request for Comments on "Results of a Workshop Meeting to Discuss Protection of Public Health and Safety During Reentry into Areas Potentially Contaminated With a Lethal Chemical Agent (GB, VX, or Mustard Agent)"

**Summary:** CDC has prepared a report on a workshop meeting to discuss protection of public health and safety during reentry into areas potentially contaminated with a lethal chemical agent (GB, VX, or Mustard Agent). Copies may be obtained from the address below. Public review and comment is invited.

**Dates:** Comments on "Results of a Workshop Meeting to Discuss Protection of Public Health and Safety During Reentry into Areas Potentially Contaminated With a Lethal Chemical Agent (GB, VX, or Mustard Agent)" must be received on or before August 20, 1998.

**Address:** Copies of the Results of the Workshop Meeting may be obtained by writing to: Linda Anderson, Chief,

Special Programs Group, Center for Environmental Health and Injury Control (F29), CDC, 1600 Clifton Road NE, Atlanta, Georgia 30333. Comments should be mailed to Director, Center for Environmental Health and Injury Control (F29), CDC, 1600 Clifton Road NE, Atlanta, Georgia 30333. Telephone: FTS: 526-4595, Commercial: (404) 423-4595.

#### SUPPLEMENTARY INFORMATION

##### Purpose and Background

An interagency steering committee, co-chaired by the Department of the Army and the Federal Emergency Management Agency, relying in part on a manual, "Reentry Planning: The Technical Basis for Offsite Recovery Following Warfare Agent Contamination" (ORNL-6029; Oak Ridge National Laboratory, Oak Ridge, TN 37831-6101) describing the technical bases for reentry decisions, prepared guidelines to assist emergency managers in developing plans for returning citizens to their homes after an evacuation caused by an unplanned release of a lethal chemical agent (GB, VX, or Mustard Agents: H, HD, HT).

On March 8 and 9, 1990, CDC hosted a workshop for a group of scientists and public officials to discuss issues related to reentry into areas potentially contaminated with lethal chemical agents. As a result of these efforts, a document titled "Results of a Workshop Meeting to Discuss Protection of Public Health and Safety During Reentry into Areas Potentially Contaminated with a Lethal Chemical Agent (GB, VX, or Mustard Agent)" has been developed.

The CDC announces the availability of the document and requests comments from interested parties prior to finalizing the document. A 45-day comment period will be established for review and comments; all comments received within the 45-day period will be considered.

Dated: July 10, 1990.

Robert L. Foster,

Acting Director, Office of Program Support,  
Centers for Disease Control

FR Doc. 90-18507 Filed 7-13-90 8:41 am

BILLING CODE 4160-10-0

National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control (CDC), Control of Ammonia Releases in Agricultural Applications; Meeting

Name: Control of Ammonia Releases in Agricultural Applications

Time and Date: 1 p.m.-5 p.m., July 31, 1990

Place: Ohio Department of Agriculture, Division of Plant Industry,

Building 1 Conference Room, 8900 E. Main Street, Reynoldsburg, Ohio 43068-3399

Status: Open to the public, limited only by the space available.

Purpose: To conduct an open meeting for the review of a NIOSH project entitled "Control of Ammonia Releases in Agricultural Applications." This project concerns the safety of agricultural anhydrous ammonia equipment and storage.

Contact Person for Additional Information: Amy A. Beatley, NIOSH, CDC, 4676 Columbia Parkway, Mailstop R5, Cincinnati, Ohio 45226, telephone 513/641-4221 or FTS 634-4221.

Dated: July 8, 1990.

Elvia Hilym,

Associate Director for Policy Coordination,  
Centers for Disease Control

FR Doc. 90-18507 Filed 7-13-90 8:41 am

BILLING CODE 4160-10-0

National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control (CDC), Analytical Method for Total Isocyanate in Air; Meeting

Name: Analytical Method for Total Isocyanate in Air

Time and Date: 1 p.m.-5 p.m., August 9, 1990

Place: Alice Hamilton Laboratory, Conference Room C, NIOSH, CDC, 5555 Ridge Avenue, Cincinnati, Ohio 45223

Status: Open to the public, limited only by the space available.

Purpose: To conduct an open meeting for the review of a NIOSH project entitled "Analytical Method for Total Isocyanate in Air." This project involves the development of an analytical method for total isocyanate group (monomeric isocyanate, prepolymeric isocyanate, polyurethane-bound isocyanate, etc.) based on the reaction of isocyanate groups with a bifunctional nucleophile.

Contact Person for Additional Information: Robert P. Streicher, NIOSH, CDC, 4676 Columbia Parkway, Mailstop R-7, Cincinnati, Ohio 45223, telephone 513/641-4295 or FTS 654-4295.

Dated: July 8, 1990.

Elvia Hilym,

Associate Director for Policy Coordination,  
Centers for Disease Control

FR Doc. 90-18507 Filed 7-13-90 8:41 am

BILLING CODE 4160-10-0

#### Food and Drug Administration

(Docket No. 90N-0163)

Health Care Plasma Center, Inc., and Medical Plasma, Inc.; Opportunity for Hearings on Proposals To Revoke U.S. License Nos. 1039 and 993

Agency: Food and Drug Administration, FDA.

#### Action Notice.

SUMMARY: The Food and Drug Administration (FDA) is announcing an opportunity for hearings on proposals to revoke the establishment licenses (U.S. License No. 1039 and 993) and the product licenses issued to Health Care Plasma Center, Inc., and Medical Plasma, Inc., respectively, for the manufacture of Source Plasma. The proposed revocations are based on the inability of authorized FDA employees to conduct inspections of these facilities which are no longer in operation.

DATES: The firms may submit written requests for hearings to the Dockets Management Branch by August 15, 1990. The firms must submit any data justifying hearings by September 14, 1990. Other interested persons may submit written comments on the proposed revocations by September 14, 1990.

ADDRESSES: Submit written requests for hearings, any data justifying hearings, and any written comments on the proposed revocations to the Dockets Management Branch (HFA-303), Food and Drug Administration, Rm. 4-62, 8600 Fishers Lane, Rockville, MD 20857.

FOR FURTHER INFORMATION CONTACT: Ann Reed Gaines, Center for Biologics Evaluation and Research (HFB-130), Food and Drug Administration, 8800 Rockville Pike, Bethesda, MD 20892-2071-225-5164.

SUPPLEMENTARY INFORMATION: FDA is initiating proceedings to revoke the establishment licenses (U.S. License No. 1039) and the product license issued to Health Care Plasma Center, Inc. with facilities at 634 Whitehall Street SW, Atlanta, GA 30312, and 2134 West Pratt St., Baltimore, MD 21223; and the establishment license (U.S. License No. 993) and the product license issued to Medical Plasma, Inc. with facilities at 171 Simpson St., Atlanta, GA 30312; and 702 South Sixth Ave., Tucson, AZ 85701; for the manufacture of Source Plasma. Proceedings to revoke the licenses issued to Health Care Plasma Center, Inc., and Medical Plasma, Inc. are being initiated because on-site inspections by FDA employees in the respective locations revealed that the facilities

# **Guidelines for Chemical Warfare Agents in Military Field Drinking Water**

COMMITTEE ON TOXICOLOGY  
NATIONAL RESEARCH COUNCIL

---

# Guidelines for Chemical Warfare Agents in Military Field Drinking Water

Subcommittee on Guidelines for  
Military Field Drinking-Water Quality


Committee on Toxicology

Board on Environmental Studies  
and Toxicology

Commission on Life Sciences

National Research Council

NATIONAL ACADEMY PRESS  
Washington, D.C. 1995



NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

The National Academy of Sciences is a private, nonprofit, self-perpetuating society of distinguished scholars engaged in scientific and engineering research, dedicated to the furtherance of science and technology and to their use for the general welfare. Upon the authority of the charter granted to it by the Congress in 1863, the Academy has a mandate that requires it to advise the federal government on scientific and technical matters. Dr. Bruce Alberts is president of the National Academy of Sciences.

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The project was supported by the U.S. Army under contract No. DAMD 17-89-C-9086.

Additional copies of this report are available from the Board on Environmental Studies and Toxicology, 2101 Constitution Avenue, N.W., Washington, D.C. 20418.

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# Preface

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**I**n 1992, the U.S. Army requested the National Research Council (NRC) to review its proposed field drinking-water-quality standards for several chemical warfare (CW) agents. The proposed standards had been developed by the Army, in collaboration with the Lawrence Livermore National Laboratory, as a defensive measure to protect the health and performance of U.S. and NATO military personnel in the event of a chemical attack.

In response to the Army's request, the NRC organized the Subcommittee on Guidelines for Military Field Drinking-Water Quality within the Committee on Toxicology. The subcommittee met several times beginning in February 1993 to address the toxicity of various CW agents, the adequacy of proposed field-water-quality standards, and the Army's assumptions in developing the field-water-quality standards. The subcommittee comprised professionals with expertise in toxicology, epidemiology, medicine, biochemistry, pathology, pharmacology, analytical chemistry, and public health. We hope that the report of this subcommittee will be useful in protecting the health and performance of U.S. and NATO military personnel.

The subcommittee was greatly assisted by several individuals who provided information on the toxicity of the CW agents considered in this report. We gratefully acknowledge Colonel Frederick Erdtmann and Colonel Eric Evenson of the U.S. Army for their interest and support of



the project. We also thank other persons who provided information for the subcommittee, including Lieutenant Colonel Gary M. Bratt (U.S. Army), Jeffery Daniels (Lawrence Livermore National Laboratory), and Stephen Schaub (U.S. Environmental Protection Agency).

We are grateful for the assistance of the NRC staff in the preparation of this report. In particular, the subcommittee wishes to acknowledge Kulbir S. Bakshi, project director for the subcommittee and program director for the Committee on Toxicology, whose hard work and expertise were most effective in bringing this report to completion. Other staff members who contributed to this effort are Paul Gilman, executive director of the Commission on Life Sciences; James J. Reisa, director of the Board on Environmental Studies and Toxicology; Carol A. Maczka, program director for toxicology and risk assessment; Ruth E. Crossgrove, editor; and Lucy Fusco, project assistant.

Last, but by no means least, the work of all the members of the subcommittee is greatly appreciated.

Ian A. Greaves, *Chair*  
Subcommittee on Guidelines for Military  
Field-Drinking Water Quality

Rogene F. Henderson, *Chair*  
Committee on Toxicology

who provided information for Colonel Gary M. Bratt (U.S. Army National Laboratory), and the Defense Agency).

NRC staff in the preparation of this report wishes to acknowledge the work of the subcommittee and program staff whose hard work and expertise were essential to the completion of this report. Other staff members are Paul Gilman, executive director; James J. Reisa, director of the Division of Toxicology; Carol A. Maczka, manager of risk assessment; Ruth E. Anderson, technical assistant.

On behalf of all the members of the subcommittee,

James J. Reisa, *Chair*  
Division of Toxicology  
Department of Defense  
Office on Guidelines for Military  
Drinking Water Quality

Ruth E. Anderson, *Chair*  
Division of Toxicology

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# *GUIDELINES FOR CHEMICAL WARFARE AGENTS IN MILITARY FIELD DRINKING WATER*

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# Executive Summary

**M**odern chemical warfare began in 1915 with the use of chlorine by Germany in a large-scale attack against the Allies near Ypres, Belgium. During World War I, almost 100,000 deaths and more than 1 million casualties were caused by the use of chemical warfare (CW) agents, such as chlorine, phosgene, and sulfur mustard. The 1925 Geneva Protocol prohibited the use of chemical and biological weapons but did not address their development, production, and storage. Unfortunately, the use of CW agents continued: they were used by Italy against Ethiopia (1935-1936), by Japan against China (1939-1944), and by Iraq against Iran and against its own Kurdish population (1983-1988). The threat of chemical warfare by Iraq was reported during the Persian Gulf War in 1991.

CW agents are generally designed to be used on opposing military forces to produce death or incapacitation. When they are used in military attacks, they are potential contaminants of field drinking-water supplies. CW agents that could appear in military field water and that are of particular concern to the Army are 3-quinuclidinyl benzilate (BZ), organophosphorus nerve agents (GA, GB, GD, and VX), sulfur mustard agents (HD, THD, and HT), T-2 toxin (a fungal metabolite), lewisite (an arsenical vesicant), and cyanide.

Military standards for field drinking-water supplies exist for all the CW agents listed above except T-2 toxin; however, comprehensive re-

view of the standards has not been performed since the 1960s. Therefore, the U.S. Army Office of the Surgeon General is updating these standards to assist the Army in protecting the health and performance of military personnel potentially exposed to toxic concentrations of CW agents in field drinking water during combat. The Army, in collaboration with the Lawrence Livermore National Laboratory, performed the following: (1) reviewed and assessed the potential adverse health effects associated with ingestion of selected CW agents, (2) defined criteria for establishing revised field drinking-water standards for each of these agents, and (3) recommended revision, as needed, to the current field drinking-water standards.

The Army requested that the National Research Council (NRC) review the toxicity of selected CW agents and assess the adequacy of its proposed field drinking-water standards. The NRC was asked to take into consideration the Army's assumptions concerning duration and amount of consumption of contaminated field drinking water. To develop consistent field drinking-water guidelines for the CW agents, the Army assumes the following regarding water-consumption rates and exposure periods:

- The maximum individual daily amount of drinking water required by military personnel to remain combat-effective ranges from 5 to 15 liters (L)/day, depending on the climate, season, and intensity of work.
- Military personnel are not expected to be exposed to CW agents for more than 7 days. Therefore, short-term (7-day) field drinking-water standards are recommended for all the CW agents.

The Army's proposed standards for short-term consumption of drinking water contaminated with CW agents are not intended for application to civilian populations and do not represent standards for drinking water treated at fixed or permanent military installations. These proposed standards assume some degree of water treatment, either by individual disinfection (iodine tablets, chlorine ampules, or boiling) or by portable devices. Some soldier-performance degradation, casualties from toxic-substance exposure, and reduced combat efficiency are to be expected in these situations.

The NRC assigned this study to the Committee on Toxicology (COT),

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ciency are to be expected in

nittee on Toxicology (COT),

which organized the Subcommittee on Guidelines for Military Field Drinking-Water Quality to evaluate the toxicity of 3-quinuclidinyl benzi-  
late, organophosphorus nerve agents, sulfur mustard agents, T-2 toxin,  
lewisite, and cyanide.

This report presents the subcommittee's evaluations of the Army's  
proposed standards. The report also presents the subcommittee's recom-  
mendations for preventing adverse health effects in military personnel  
exposed to CW agents in field drinking water and for improving the tox-  
icity data base for these CW agents. It should be noted that the intent of  
this report was not to review the toxicity of the CW agents in detail but  
to determine the adequacy of the Army's proposed field drinking-water  
standards. For greater detail on the toxicity of the CW agents, the read-  
er is referred to the reports of the Lawrence Livermore National Labora-  
tory and the U.S. Army.<sup>1</sup>

The subcommittee's recommendations on acceptable exposure levels  
of CW agents in field drinking water for military personnel are referred  
to as "guidelines" rather than "standards." The subcommittee believes  
that the use of the term "guidelines" provides the necessary flexibility to

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<sup>1</sup>Lawrence Livermore National Laboratory. February 1988. Evaluation of  
Military Field-Water Quality, Vol. 4, Part 1, J.I. Daniels, ed. Publ. No. AD  
UCRL-21008. Report prepared for the U.S. Army Medical Research and  
Development Command, Fort Detrick, Frederick, Md.

Lawrence Livermore National Laboratory. January 1990. Evaluation of  
Military Field-Water Quality, Vol. 4, Part 2, J.I. Daniels, ed. Publ. No. AD  
UCRL-21008. Report prepared for the U.S. Army Medical Research and  
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Field-Water Quality, Vol. 1, Executive Summary, J.I. Daniels and G.M.  
Gallegos, eds. Publ. No. AD UCRL-21008. Report prepared for the U.S. Army  
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U.S. Army. 1988. Recommended Field Drinking Water Criteria for  
Chemical Agent Sulfur Mustard. Technical Report 8816. U.S. Army Biomedical  
Research and Development Laboratory, Fort Detrick, Frederick, Md.

U.S. Army. 1990. Field-Water Quality Standards for BZ. Technical Report  
9001. U.S. Army Biomedical Research and Development Laboratory, Fort  
Detrick, Frederick, Md.

field commanders who must weigh the application of exposure recommendations against the need for adequate hydration, combat readiness, and mission success. The term "standards" implies a regulatory limit that cannot be exceeded.

The subcommittee reviewed the Army's criteria for developing field drinking-water standards and generally agrees with the criteria. Therefore, the subcommittee did not develop its own criteria for establishing guidelines for CW agents in military field drinking water.

The toxicity of the CW agents and the adequacy of the Army's proposed field drinking-water standards are summarized in the following sections; the subcommittee-recommended field drinking-water guidelines for CW agents are also presented.

The subcommittee judged that acute adverse health effects and performance-degrading effects among military personnel are the most relevant toxicity end points for deriving field drinking-water guidelines for short-term exposures of 7 days or less. The possibility of carcinogenic effects from exposures of less than 7 days is remote. However, the report calls attention to data on the potential carcinogenicity or genotoxicity whenever it is applicable.

The subcommittee notes that the physical reactions, such as hydrolysis or oxidation, and the poor solubility of most of the CW agents all reduce the potential for exposure via ingestion. The exposure guidelines do not take into account the potential reduction in exposure due to the physical reactions and poor solubility and therefore are even more protective of health.

#### AGENT BZ

Agent BZ (3-quinuclidinyl benzilate) produces profound hallucinogenic effects in humans. Production of BZ was terminated in 1964 because of the realization that its effects on front-line troops would be varied and unpredictable (thus the term "buzz" or Agent BZ). Toxic effects from oral exposure to BZ include rapid pulse, dry mouth, blurred vision, poor coordination, stupor, confusion, hallucinations, paresthesia of the legs, weakness, speech difficulties, and tremors of the face and arms.

Sufficient human toxicity data are available for BZ to set standards for field drinking water. In one study, heart rate, blood pressure, disorientation, and delirium were evaluated following oral administration of BZ to



ation of exposure recommendations, combat readiness, and a regulatory limit that

criteria for developing field standards with the criteria. Therefore, the criteria for establishing drinking water.

adequacy of the Army's program is summarized in the following drinking-water guidelines

adverse health effects and personnel are the most relevant drinking-water guidelines for the possibility of carcinogenic effects. However, the recommendation of carcinogenicity or genotoxicity

actions, such as hydrolysis of the CW agents all reduce exposure guidelines do not correspond to the physical and chemical properties of a more protective of

induces profound hallucinations was terminated in 1964 because front-line troops would be vulnerable to Agent BZ. Toxic effects include dry mouth, blurred vision, tremors, paresthesia of the fingers of the face and arms.

For BZ to set standards for blood pressure, disorientation, and oral administration of BZ to

healthy male volunteers. The no-observed-adverse-effect level (NOAEL) for BZ was estimated to be 0.5 microgram per kilogram ( $\mu\text{g/kg}$ ) of body weight. For a person weighing 70 kg, the NOAEL is equivalent to 35  $\mu\text{g/day}$ . Based on a NOAEL of 35  $\mu\text{g/day}$ , the Army recommended field drinking-water standards for BZ of 2.3  $\mu\text{g/L}$  and 7  $\mu\text{g/L}$ , assuming a water consumption of 15 L/day and 5 L/day, respectively. The subcommittee is in agreement with the Army's proposed standards. Therefore, the subcommittee's recommended field drinking-water guidelines for BZ are the same as the Army's proposed standards.

## ORGANOPHOSPHORUS NERVE AGENTS

Organophosphorus nerve agents have been used as CW agents for over 50 years. Those of current concern are tabun (Agent GA), sarin (Agent GB), soman (Agent GD), and Agent VX. These synthetic chemicals are among the most acutely toxic substances known.

Symptoms and signs of acute toxicity of organophosphorus nerve agents include excessive bronchial, salivary, ocular, and intestinal secretions. Other symptoms and signs are sweating, bronchospasm, diarrhea, slow heart beat, muscle fasciculation, twitching, weakness, paralysis, loss of consciousness, tension, anxiety, restlessness, convulsion, and depression of central respiratory drive.

Organophosphorus nerve agents bind the enzyme acetylcholinesterase (AChE) and inactivate it, thereby allowing accumulation of large amounts of acetylcholine at neural synapses and neuroeffector junctions. Toxic effects of organophosphorus nerve agents have been largely attributed to inhibition of AChE. Even though there is a relationship between organophosphate toxicity and AChE inhibition, this relationship is not sufficiently precise to predict the risk to humans exposed at low concentrations. There is a need to augment enzyme-inhibition data with other measures of chemical exposure to develop more accurate health guidelines. Such measures are currently unavailable; thus, the use of AChE inhibition data is the only available alternative.

The Army's proposed standards for organophosphorus nerve agents, based on modeled estimates of 50% AChE inhibition following GD exposure, are 4  $\mu\text{g/L}$  and 12  $\mu\text{g/L}$  for a water consumption of 15 L/day and 5 L/day, respectively. The subcommittee, however, disagrees with

the Army's approach of using 50% AChE inhibition as the basis for the standards. Clinical signs and symptoms of toxicity of organophosphorus nerve agents have been reported to occur in some individuals at 50% inhibition of AChE. In addition, a 50% inhibition of AChE might be associated with performance degradation in healthy adults. To accommodate for the biological variability inherent in red-blood-cell acetylcholine measurements (up to a 2-fold difference) and the possibility of confounding effects from exposure to other anticholinesterase chemicals, to assure against decreased battlefield performance, and to protect previously sensitized individuals, the subcommittee selected an AChE inhibition level of 25% as a definite NOAEL. It should be noted that the lowest level of statistical reliability in measuring AChE changes is approximately 20%; changes that are less than 20% cannot be detected reliably.

Based on the available data, the subcommittee recommends that the 25% AChE inhibition level be used as the basis for the field drinking-water guidelines for organophosphorus nerve agents and recommends the following guidelines for the organophosphorus nerve agents: GA, 22.5  $\mu\text{g/L}$  and 70.0  $\mu\text{g/L}$ ; GB, 4.6 and 13.8  $\mu\text{g/L}$ ; GD, 2.0 and 6.0  $\mu\text{g/L}$ ; and VX, 2.5 and 7.5  $\mu\text{g/L}$ —assuming a water consumption of 15 and 5 L/day, respectively. The subcommittee concludes that these guidelines are appropriate until the results of future research indicate that 25% AChE inhibition is inadequate or overly conservative.

### SULFUR MUSTARD AGENTS

Three sulfur mustard agents are found in CW arsenals: Agent HD (distilled sulfur mustard), Agent THD (HD to which an acryloid copolymer (T) is added as a thickener to increase its viscosity), and Agent HT (a combination of 60% HD and 40% T, which lowers the freezing point of the mixture).

The sulfur mustard agents are vesicants, causing blistering on exposed skin and mucous membranes, and are lethal at high doses. No controlled studies on human ingestion of sulfur mustard agents exist in the literature. Gastrointestinal irritation is considered the primary toxic effect following ingestion of low concentrations of sulfur mustard compounds in drinking water.

The literature on the toxicity of sulfur mustard agents primarily con-

hibition as the basis for the toxicity of organophosphorus in some individuals at 50% inhibition of AChE might be healthy adults. To account for red-blood-cell acetylcholinesterase and the possibility of concholinesterase chemicals, tolerance, and to protect previously selected an AChE inhibitor should be noted that the low AChE changes is approximately cannot be detected reliably. The committee recommends that the basis for the field drinking-water agents and recommends phosphorus nerve agents: GA, 3.8 µg/L; GD, 2.0 and 6.0 µg/L. Assuming a water consumption of 15 L/day, it concludes that these guidelines are conservative. Research indicates that 25% reserve.

## AGENTS

in CW arsenals: Agent HD (to which an acryloid copolymer is added to increase its viscosity), and Agent HT (which lowers the freezing point and causes blistering on exposed skin at high doses. No controlled studies of these agents exist in the literature. The primary toxic effect of sulfur mustard compounds in humans is caused by mustard agents primarily con-

tains information on the toxicity of HD. The subcommittee assumed that the toxicity of the other sulfur mustard agents—THD and HT—is similar to that of HD.

In a subchronic-toxicity study, rats were administered HD by gavage at doses ranging from 0.0033 to 0.3 mg/kg of body weight. Epithelial hyperplasia of the forestomach was observed in the 0.3-mg/kg group. The no-observed-effect level (NOEL) was estimated to be 0.1 mg/kg/day. Based on that NOEL in rats, the subcommittee recommends field drinking-water guidelines for HD of 47 µg/L and 140 µg/L, assuming a water consumption of 15 L/day and 5 L/day, respectively. The subcommittee's recommended guidelines for sulfur mustard are the same as the Army's proposed standards.

For an exposure lasting 7 days in a lifetime of a person, the increased risk of cancer from exposure to HD at 140 µg/L, assuming a water consumption of 5 L/day, is calculated to be  $4.1 \times 10^{-5}$ . However, given the limited solubility of HD in water, the resulting dose and thus the actual risk might be considerably less.

It is not known how much excess chlorination or iodination is needed to degrade various concentrations of sulfur mustard in raw water. It is possible that disinfectant materials currently used to treat field drinking water substantially reduce concentrations of sulfur mustard. The subcommittee recommends that this approach for reducing sulfur mustard in water be further investigated.

## T-2 TOXIN

T-2 toxin is a mycotoxin and a metabolite of several species of fungi. T-2 toxin has been implicated as a CW agent in Southeast Asia and Afghanistan. Data on the toxicity of T-2 toxin in animals and humans are limited. Diacetoxyscirpenol (DAS)—also a mycotoxin—is structurally similar to T-2 toxin, and the toxicity data on DAS are substantial because of its use as an antineoplastic drug. Although the data on T-2 toxin in humans are limited, they do indicate that the toxic effects of T-2 toxin are similar to those of DAS. Therefore, DAS is used as a surrogate for T-2 toxin. DAS has been administered in 5-day clinical trials for treatment of cancer in patients who have not responded to other forms of therapy. The most common toxic effects of DAS in cancer patients are

nausea and vomiting. Less common effects are myelosuppression, hypotension, diarrhea, central nervous system dysfunction, and fever and chills. The mechanism through which DAS and T-2 toxin cause toxicity is through the inhibition of protein synthesis.

The Army's proposed field drinking-water standards for T-2 toxin are based on a NOEL of 2.6  $\mu\text{g}/\text{kg}$  of body weight per day for DAS in clinical trials. Adjustments were made for the time difference between the 7-day field conditions and the 5-day clinical trials. The subcommittee concludes that the Army's proposed standards of 8.7  $\mu\text{g}/\text{L}$  for a water consumption of 15 L/day and 26  $\mu\text{g}/\text{L}$  for a water consumption of 5 L/day are appropriate. The subcommittee's recommended field drinking-water guidelines for T-2 toxin are the same as the Army's proposed standards.

The current field-test kit for detecting T-2 toxin in water has a detection limit of 470  $\mu\text{g}/\text{L}$ , which is above the field drinking-water guidelines of 8.7 or 26  $\mu\text{g}/\text{L}$  recommended by the subcommittee. Therefore, the subcommittee recommends that a field-test kit capable of detecting T-2 toxin at or below the guideline concentrations be developed and made available to soldiers.

### LEWISITE

Lewisite is an outdated organoarsenical CW agent. However, it might still be encountered on the battlefield. On contact with the skin or mucous membranes, it causes an intense inflammatory reaction and produces burns and blistering. Lewisite is also a lung irritant and a systemic poison.

Despite the relative longevity of lewisite as a CW agent, the available toxicological data on human and animal exposure are sparse. No human data are available relating to ingestion of lewisite. However, substantial human data are available on the health effects of trivalent arsenic, which is the form of arsenic present in lewisite. Ingestion of arsenic causes gastrointestinal irritation and pain.

The Army's recommended standards for lewisite in field drinking water were proposed on the basis of developmental toxicity studies in rats and rabbits administered lewisite by gavage. The NOELs in rats and rabbits were estimated to be 1.5 mg/kg and 0.016 mg/kg of body weight per day, respectively. Therefore, the lowest NOEL—0.016 mg/kg/day

re myelosuppression, hypofunction, and fever and T-2 toxin cause toxicity

standards for T-2 toxin are 10 µg per day for DAS in clinical trials. The difference between the 7- and 10-µg/L standards is 3 µg/L. The subcommittee confirms 8.7 µg/L for a water consumption of 5 L/day and recommended field drinking-water standards for the Army's proposed standards.

T-2 toxin in water has a detected drinking-water guidelines subcommittee. Therefore, the subcommittee is capable of detecting T-2 toxin and be developed and made

(or 16 µg/kg/day) in the rabbit developmental toxicity study—was selected to derive the field drinking-water standards for lewisite. The arsenic fraction in 16 µg of lewisite is 5.8 µg. Based on a NOEL of 5.8 µg/kg/day, the Army proposed standards for arsenic (in lewisite) of 80 µg/L and 27 µg/L, assuming a water consumption of 5 L/day and 15 L/day, respectively.

The subcommittee concludes that the Army's proposed standards for lewisite (based on its arsenic fraction) are appropriate. Therefore, the subcommittee's recommended field drinking-water guidelines for lewisite are the same as the Army's proposed standards.

At present, there is no field drinking-water monitoring capability that can reliably detect lewisite or elemental arsenic at the recommended field drinking-water guidelines. Therefore, the subcommittee recommends that field monitoring techniques for low-level detection of arsenic or lewisite be developed.

## CYANIDE

Cyanide has been known as a potent toxicant for over 200 years. Hydrogen cyanide gas was used as a CW agent by France during World War I. Typical symptoms of acute exposure of humans to sublethal doses of cyanide are headache, nausea, weakness, palpitations, tremors, and breathlessness. The nervous and respiratory systems are the first to fail in severe cyanide poisoning. When exposure is sufficiently high, death results from respiratory arrest.

The mechanism of cyanide toxicity involves inhibition of enzymes for cellular respiration. Blood cyanide concentrations have been correlated with various health effects. The most reliable data are the measured concentrations of cyanide in blood drawn from patients who received infusions of sodium nitroprusside (a cyanide-releasing drug) during surgery. On the basis of those data, a blood cyanide concentration of 0.5 mg/L is considered nontoxic. By using a pharmacokinetic model and assuming that the blood cyanide concentration of 0.5 mg/L is nontoxic, the Army proposed field drinking-water standards for cyanide of 2 mg/L and 6 mg/L, assuming a water consumption of 15 L/day and 5 L/day, respectively. The subcommittee is in agreement with the Army's proposed standards. Therefore, the subcommittee's recommended field

of agent. However, it might contact with the skin or mucous membrane, causing a local inflammatory reaction and prolonged irritant and a systemic

As a CW agent, the available data are sparse. No human data are available. However, substantial data are available on the toxicity of trivalent arsenic, which is a CW agent. Ingestion of arsenic causes

of lewisite in field drinking-water standards. The NOELs in rats and mice are 0.016 mg/kg of body weight and 0.016 mg/kg/day, respectively. The NOEL—0.016 mg/kg/day

drinking-water guidelines for cyanide are the same as the Army's proposed standards.

### CONCLUSIONS

Table E-1 summarizes the subcommittee's recommended field drinking-water guidelines for BZ; organophosphorus nerve agents GA, GB, GD, and VX; sulfur mustard; T-2 toxin; lewisite; and cyanide.

The Army has indicated that it plans to submit the subcommittee's recommended field drinking-water guidelines for the CW agents to a triservice (Army, Navy, and Air Force) medical review panel for formal adoption. If adopted, they will be used to develop joint service standards. These field drinking-water standards might then be submitted for incorporation into the North Atlantic Treaty Organization's Standardization Agreements and the Quadripartite Standardization Agreements.

**TABLE E-1** Summary of the Subcommittee's Recommended Field Drinking-Water Guidelines for Selected CW Agents in Field Drinking Water<sup>a</sup>

CW Agent	Recommended Guidelines	
	5 L/day	15 L/day
BZ ( $\mu\text{g/L}$ )	7.0	2.3
Organophosphorus nerve agents		
Agent GA ( $\mu\text{g/L}$ )	70.0	22.5
Agent GB ( $\mu\text{g/L}$ )	13.8	4.6
Agent GD ( $\mu\text{g/L}$ )	6.0	2.0
Agent VX ( $\mu\text{g/L}$ )	7.5	2.5
Sulfur mustard ( $\mu\text{g/L}$ )	140.0	47.0
T-2 toxin ( $\mu\text{g/L}$ )	26.0	8.7
Lewisite ( $\mu\text{g/L}$ ) (arsenic fraction) <sup>b</sup>	80.0	27.0
Cyanide (mg/L)	6.0	2.0

<sup>a</sup>Assumes a water consumption of up to 7 days.

<sup>b</sup>Based on detection of the arsenic fraction of lewisite in water; the corresponding concentration of lewisite is about 2.75 times greater.

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ended Guidelines	
	15 L/day
	2.3
	22.5
2000	4.6
	2.0
	2.5
	47.0
	8.7
	27.0
	2.0

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mes greater.

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Introduction

Modern chemical warfare began in 1915 with the use of chlorine by Germany in a large-scale attack against the Allies near Ypres, Belgium. That incident during World War I led to increased efforts toward the development of more toxic chemical warfare (CW) agents (e.g., agents that are toxic following dermal absorption) as well as more effective protective gear (e.g., more effective gas masks). In July 1917, the blistering agent sulfur mustard was used by the German army for the first time as a CW agent (IOM, 1993). Almost 100,000 deaths and more than 1 million casualties were caused by the use of CW agents in World War I. The 1925 Geneva Protocol prohibited the use of chemical and biological weapons but did not address their development, production, and storage. Unfortunately, the use of CW agents continued. There is strong evidence that they were used by Italy against Ethiopia (1935-1936), by Japan against China (1939-1944), and by Iraq against Iran as well as against the Kurdish population (1983-1988). The threat of chemical warfare by Iraq was reported during the Persian Gulf War in 1991. Therefore, CW agents are considered possible contaminants of field drinking-water supplies for military personnel during military conflicts (Lawrence Livermore National Laboratory, 1990a).

CW agents that might appear in field drinking water following a military attack include 3-quinuclidinyl benzilate (BZ), organophosphorus

nerve agents (GA, GB, GD, and VX), sulfur mustard agents, T-2 toxin (a fungal metabolite recently identified as a possible CW agent), lewisite (an arsenical vesicant), and cyanide. Other CW agents might also contaminate water supplies, but this report reviews the toxicity and drinking-water standards of only the CW agents listed above.

Because of the Army's concern for the potential exposure of military personnel to CW agents, the Army requested that the National Research Council (NRC) review the toxicity of the CW agents and assess the appropriateness of the proposed field drinking-water-quality standards for these agents. Most of the standards were proposed by the Army in collaboration with the Lawrence Livermore National Laboratory (1988, 1990a,b). The Army's recommended standards for the CW agents of concern are applicable only to military personnel deployed in the field. They are meant to protect military personnel against acute adverse health effects or performance-degrading effects resulting from the ingestion of contaminated field drinking water. The Army's assumptions in deriving short-term field drinking-water standards are that military personnel consume 5-15 liters (L) of water per day, that they might be exposed for up to 7 days, and that the field drinking water contains no other toxic materials.

The NRC assigned this task to the Committee on Toxicology (COT). COT's Subcommittee on Guidelines for Military Field Drinking-Water Quality reviewed and assessed (1) the potential health effects associated with ingestion of each of the CW agents of concern, and (2) the Army's criteria for establishing revised field drinking-water standards. Based on the review, the subcommittee determined the adequacy of the field drinking-water standards for the CW agents of concern and recommended revisions, as needed, to those standards. In addition, the NRC was asked to take into consideration the Army's assumptions concerning consumption of contaminated field drinking water and duration of exposure. Neither the existence or performance of water-quality monitoring devices nor the efficiency of water-purification equipment was a consideration in the subcommittee's recommendations for field drinking-water guidelines for CW agents. Similarly, the recommended guidelines are not intended to protect against late-appearing health effects such as carcinogenesis or teratogenesis. However, the report calls attention to data on potential carcinogenicity or genotoxicity whenever it appears that such data would be useful to field commanders.



mustard agents, T-2 toxin (possible CW agent), lewisite CW agents might also consider the toxicity and drinking-water above.

potential exposure of military personnel that the National Research Council (NRC) review CW agents and assess the appropriate water-quality standards for proposed by the Army in collaboration with the National Research Laboratory (1988, 1990a,b) standards for the CW agents of concern for personnel deployed in the field. The report also discusses the potential for acute adverse health effects resulting from the ingestion of CW agents. The NRC's assumptions in deriving the standards for military personnel convey that military personnel convey might be exposed for up to 30 days. The report contains no other toxic mate-

Committee on Toxicology (COT). The report also discusses the potential for acute adverse health effects associated with the ingestion of CW agents, and (2) the Army's water standards. Based on the adequacy of the field standards of concern and recommendations. In addition, the NRC's assumptions concerning water and duration of exposure of water-quality monitoring on equipment was a consideration for field drinking-water standards. The recommended guidelines are based on health effects such as cancer. The report calls attention to data gaps whenever it appears that there are gaps.

In this report, the subcommittee's recommendations on acceptable exposure levels for CW agents in field drinking water are referred to as "guidelines" rather than "standards" for field drinking-water quality. The term "standards" implies a regulatory limit that cannot be exceeded.

The subcommittee believes that the use of the term "guidelines" provides the necessary flexibility to field commanders who must weigh the application of exposure recommendations against the need for adequate hydration, combat readiness, and mission success.

The subcommittee reviewed the Army's criteria for developing field drinking-water standards and generally agrees with the criteria (see Appendix A). Therefore, the subcommittee did not develop its own criteria for establishing guidelines for CW agents in military field drinking water.

Field drinking-water guidelines recommended for the CW agents by the subcommittee are intended to protect essentially all military occupational specialties. The recommended guidelines are not applicable to populations of civilians and do not represent water-quality standards for drinking water treated at fixed water-purification installations. It should be noted that the intent of this report was not to review the toxicity of the CW agents in detail but to determine the adequacy of the Army's proposed field drinking-water standards. For greater detail on the toxicity of the CW agents, the reader is referred to the reports of the Lawrence Livermore National Laboratory (1988, 1990a,b) and the U.S. Army (1988, 1990a).

The Army has indicated that it plans to submit the NRC's field drinking-water guidelines to a triservice (Army, Navy, and Air Force) medical review panel for formal adoption as joint service standards. The standards might then be submitted for incorporation into the North Atlantic Treaty Organization's Standardization Agreements and the Quadripartite Standardization Agreements.

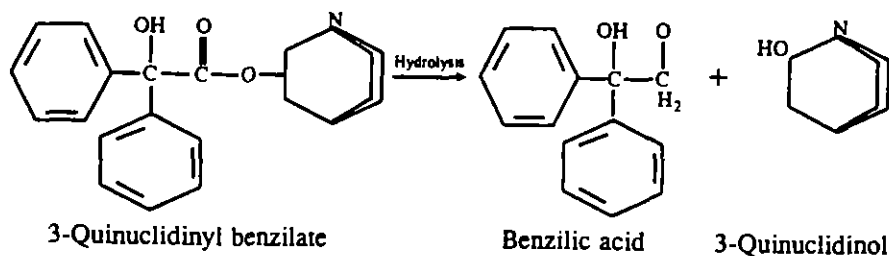
The report is organized as follows: 3-quinuclidinyl benzilate (BZ) is discussed in Chapter 2, organophosphorus nerve agents in Chapter 3, sulfur mustard in Chapter 4, T-2 toxin in Chapter 5, lewisite in Chapter 6, and cyanide in Chapter 7. Appendix A describes the criteria used by the Army to establish field drinking-water standards and the subcommittee's evaluation of the criteria. Appendix B contains a discussion on the current capability to detect CW agents in field drinking water.

## Guidelines for 3-Quinuclidinyl Benzilate

### INTRODUCTION

The chemical 3-quinuclidinyl benzilate (BZ) is a bicyclic ester and exists as a crystalline solid. At high doses, it has pronounced hallucinogenic effects. BZ was produced in the United States between 1962 and 1964, but production was terminated because of the realization that BZ's effects on front-line troops could be varied and unpredictable (thus the term "buzz" or Agent BZ). In the United States, existing amounts of BZ are thought to equal only a few grams (Compton, 1988). Field drinking-water-quality standards for BZ have been proposed by Palmer (1990).

Studies regarding the solubility and hydrolysis of BZ indicate that BZ can hydrolyze in alkaline solution ( $\text{pH} > 11$ ) to benzylic acid and 3-quinuclidinyl within minutes (Sass et al., 1960; Yurow et al., 1963; Rosenblatt et al., 1977). This reaction is depicted below:



## TOXICITY

Sim (1961) and Ketchum et al. (1967) have described the toxic manifestations of BZ in humans. Like atropine, it inhibits the action of acetylcholine by binding to the acetylcholinesterase receptor. However, it is more potent. There is evidence that antimuscarinic drugs, such as BZ, cause hallucinogenic effects by binding to a serotonin receptor subtype (Battaglia and De Souza, 1989). Atropine-like effects include rapid pulse, dry mouth, blurred vision due to pupillary dilation, inability to solve problems or remember numbers, poor coordination, stupor, confusion, and disorientation. Paresthesia of the legs, weakness and tightness, speech difficulty, tremor of the face and arms, and tachycardia are also common symptoms.

BZ is hydrolyzed in alkaline solutions to benzylic acid and 3-quinuclidinyl. Studies in mice indicate that BZ is much more toxic than its hydrolysis products. LD<sub>50</sub>s in mice for BZ, benzylic acid, and 3-quinuclidinyl were found to be 18-25 mg/kg, >400 mg/kg, and 179 mg/kg, respectively (McNamara, 1963a). BZ has similar effects in humans and animals. With increased doses, there is increased heart rate, impaired performance, prostration, convulsion, and death rate. In a 42-day exposure of dogs administered BZ intravenously at 100 µg/kg, slight pathological changes were observed in the gastrointestinal tract (ulceration and bloody stool) in 50% of the exposed dogs and 25% of the controls. There was a slight increase in kidney weight and a slight decrease in liver and spleen weights. There were no changes in white-blood-cell or sodium measurements (McNamara, 1963b).

## FIELD DRINKING-WATER STANDARDS

There are sufficient human data on BZ to establish field drinking-water standards. In several studies, humans were administered BZ either in drinking water or by intramuscular (i.m.) injection; the doses ranged from 2 to 7 µg/kg of body weight (Sim, 1961; Avellino, 1963; Ketchum, 1963; McNamara, 1963b; Kitzes and Vancil, 1965; Ketchum et al., 1967). Animal data support human findings.

For purposes of establishing field drinking-water-quality standards for BZ, the most pertinent investigations are those of Avellino (1963) and

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enzylic acid and 3-quinucli-  
uch more toxic than its hy-  
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00 mg/kg, and 179 mg/kg,  
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## STANDARDS

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Ketchum (1963). Avellino examined the available literature for data regarding potability standards for BZ in water supplies. Avellino also examined the unpublished reports ("Human Studies with BZ and Related Compounds," March, 1963) of Major James S. Ketchum, who personally supervised the administration of BZ to healthy male volunteers (Avellino, 1963). In those investigations, four subjects were administered BZ i.m. in daily doses of 0.5  $\mu$ g/kg on days 1 through 5 and on day 8, for a total of six doses in 8 days. Changes in heart rate or blood pressure (objective criterion) and symptoms of disorientation or delirium (subjective criterion) were evaluated. It was the opinion of all medical and nursing personnel who supervised the four subjects that at no time during or after the study were there any additional signs or symptoms beyond the usual BZ effects. At the termination of the study, the subjects had certain mild medical conditions that might or might not have been related to BZ administration. Those medical conditions included dermatosis (subject Je), dysphagia with mild malaise (subject We), rash (subject Ba), and low-grade fever (subject Mc) (Avellino, 1963).

Ketchum stated that the highest dose that can be absorbed without noticeable effects is 0.5  $\mu$ g/kg (Avellino, 1963). Thus, the 0.5- $\mu$ g/kg dose can be considered a no-observed-adverse-effect level (NOAEL). Ketchum also compared an oral dose of BZ to an i.m. injection in adult males and determined that the effectiveness of the oral route is approximately 75% that of an i.m. injection (Avellino, 1963). It should be noted that the number of subjects receiving the 0.5- $\mu$ g/kg i.m. dose of BZ was small (four subjects). There were mild flu-like clinical symptoms noted in the study. Neither the investigator nor the nurse felt that the symptoms resulted from the drug administration. Furthermore, because the likely route of exposure to BZ for military personnel is drinking water, as opposed to an i.m. injection, the dose of 0.5  $\mu$ g/kg via the oral route should be less adverse because 25% less BZ is absorbed (Avellino, 1963).

## SUMMARY

There is no information in the literature concerning the in vivo half-life of BZ. As mentioned previously, BZ can hydrolyze in alkaline

solutions. It is recommended that information be obtained about the fate of BZ in water.

The Army's field drinking-water standards for BZ are based on human studies. The criterion set by the Army Medical Department assumes water consumption ranging from 5 to 15 L/day, depending on climatic conditions. The duration of exposure is set at 7 days or less. The "acceptable" dose (i.e., an apparent NOAEL) for BZ is 0.5  $\mu\text{g}/\text{kg}$ , which, when normalized for a 70-kg soldier, is equivalent to 35  $\mu\text{g}/\text{day}$ . Therefore, the Army's proposed standards for a water consumption of 5 L/day or 15 L/day (for no longer than 7 days) are 7 or 2.3  $\mu\text{g}/\text{L}$  of water, respectively. No further allowance was made for individual variability because the military population is considered to be healthy with no preexisting health conditions. The allowable maximum total intake for 7 days would be 245  $\mu\text{g}$  (7 days at 35  $\mu\text{g}/\text{kg}/\text{day}$ ).

#### FIELD DRINKING-WATER GUIDELINE COMPUTATIONS

$$0.5 \mu\text{g}/\text{kg} \times 70 \text{ kg} = 35.0 \mu\text{g}.$$

Assuming a water consumption of 5 or 15 L/day, the proposed field drinking-water standards are

$$\begin{aligned} 5\text{-L consumption} &= 35.0 \mu\text{g}/5 \text{ L} = 7 \mu\text{g}/\text{L}. \\ 15\text{-L consumption} &= 35.0 \mu\text{g}/15 \text{ L} = 2.3 \mu\text{g}/\text{L}. \end{aligned}$$

#### CONCLUSIONS AND RECOMMENDATIONS

The subcommittee concludes that the Army's recommended field drinking-water standards of 2.3  $\mu\text{g}/\text{L}$  for 15 L/day of water consumption and 7  $\mu\text{g}/\text{L}$  for 5 L/day of water consumption are appropriate. The field drinking-water guidelines recommended by the subcommittee for BZ are the same as the Army's proposed standards. The subcommittee also recommends that further research be done to study the fate of BZ in water as well as the hydrolysis products of BZ after standard field-water treatment (e.g., chlorination, iodination, and boiling).

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### 3

## *Guidelines for Organophosphorus Nerve Agents*

### INTRODUCTION

**T**he organophosphorus nerve agents have been used as chemical warfare agents for over 50 years (Dunn and Sidell, 1989; Somani, 1992). This class of compounds includes tabun (Agent GA), sarin (Agent GB), soman (Agent GD), and Agent VX. These agents are lipid-soluble organic compounds that rapidly inhibit the enzyme acetylcholinesterase (AChE), and AChE inhibition leads to inhibition of nerve-muscle impulse transmission. In addition to phosphorus, organophosphorus nerve agents contain cyanide (GA), fluoride (GB and GD), or sulfur (VX).

Daniels (1990a) compiled a detailed review of the properties and fate of organophosphorus nerve agents and their health effects in animals and humans. Because of its volatility, GB is an effective toxicant by the inhalation route, whereas the relatively low volatility of VX makes it more effective following dermal exposures. All four compounds are toxic by ingestion, but only GB and VX have been thoroughly investigated for their fate in water. GB is soluble in water and dissolves rapidly (Epstein, 1974). GB hydrolysis to two strong acids, isopropyl methylphosphonic acid and hydrofluoric acid, is dependent on pH. At increased pH levels (between 6.5 and 14), hydrolysis is mediated by hydroxide-ion catalysis. However, the hydrolysis rate of GB is at a

minimum at pH levels of 4-6.5, where the reaction occurs between GB and water molecules. Increasing the temperature accelerates the hydrolysis process; however, the temperature effect will be greater for hydrolysis under alkaline conditions than for hydrolysis under acidic conditions (Epstein, 1974). Somani (1992) lists the half-lives of VX and GB (at 25°C) as 350 days and 5.4 hr, respectively. VX hydrolyzes in water very slowly and therefore is more stable in water than GB. Information on the solubility of GD is limited; it might be more persistent in water than GB. Like that of GB, a principal hydrolysis product of GD is reported to be hydrofluoric acid. There is little information on the solubility of GA.

Data on the toxicity of the hydrolysis products of GB suggest that the toxicity is negligible; at 200 ppm, the products were not toxic. Performance degradation would be unlikely to occur in military personnel consuming field water containing these products over a 7-day exposure period (Epstein, 1974; Daniels, 1990a). The toxicity of the hydrolysis products of VX has not been studied in detail. A report prepared by Small (1983) summarizes the toxicological data of the two hydrolysis products of VX that might occur in water (i.e., bisdiisopropylaminoethylaminosulfide and *S*-diisopropylaminoethyl methylphosphonic acid). The limited data suggest that hydrolysis of VX to these products does not necessarily mean that water containing these products will be potable. Consequently, water that has been contaminated with VX should always be treated before consumption by military personnel. Data on the toxicity of the hydrolysis products of GA or GD are not available.

### TOXICITY

The organophosphorus nerve agents are among the most toxic synthetic substances. The 24-hr LD<sub>50</sub>s (via the subcutaneous route) range from 20-165 µg/kg for soman to 43-158 µg/kg for sarin in laboratory animals, such as rabbits, guinea pigs, and mice. By comparison, organophosphorus insecticides, such as parathion, guthion, and malathion, are toxic only at doses exceeding tens to thousands of milligrams per kilograms. Toxic effects observed in humans and animals acutely exposed to organophosphorus nerve agents are excessive bronchial, salivary, ocu-

reaction occurs between GB and water, the rate of hydrolysis will be greater for hydrolysis under acidic conditions. The half-lives of VX and GB in water are 10 and 100 days, respectively. VX hydrolyzes in water more slowly than GB. Information is more persistent in water. The hydrolysis product of GD is re-information on the solubility

of GB suggest that the products were not toxic. Performance in military personnel consists over a 7-day exposure period. The toxicity of the hydrolysis product is detailed. A report prepared by the data of the two hydrolysis products (i.e., bisdiisopropylaminoethyl methylphosphonic acid). Exposure to these products does not mean the products will be potable. Personnel exposed to VX should always be monitored. Data on the toxicity are not available.

Among the most toxic synthetic subcutaneous route range from 0.1 to 100 mg/kg for sarin in laboratory mice. By comparison, organophosphorus pesticides, such as diazinon, malathion, and parathion, are administered in doses of milligrams per kilogram and animals acutely exposed show bronchial, salivary, ocu-

lar, and intestinal secretions. Other responses are sweating, bronchospasm, intestinal hypermotility, bradycardia, muscle fasciculations, twitching, weakness, paralysis, loss of consciousness, tension, anxiety, restlessness, insomnia, convulsions, and depression of central respiratory drive (Namba et al., 1971; Murphy, 1975; Rickett et al., 1987; Dunn and Sidell, 1989).

The route and rate of exposure strongly influence the intensity and duration of action of the organophosphorus nerve agents. The inhalation route is associated with the greatest toxicity. Inhalation of vapors or aerosols can result in toxic effects within seconds to 5 min of exposure (Somani, 1992). After percutaneous exposure to a large amount of agent (an LD<sub>50</sub> or greater), enzyme inhibition and onset of effects occur within 1-30 min—the time being inversely related to the amount of agent (Somani, 1992).

## EXPOSURE AND BIOLOGICAL MONITORING

There is a relationship between the toxicity of organophosphorus nerve agents and AChE inhibition. However, data are insufficient to predict the risk accurately in humans exposed to low doses of these nerve agents, and since most investigators use AChE inhibition as a measure of exposure rather than more direct measures, there are multiple sources of uncertainty.

The World Health Organization reports that a 50-70% reduction of plasma or red-blood-cell-AChE activity in workers exposed to organophosphate pesticides justifies the removal of workers from further exposure (WHO, 1975). Gage (1967) argues that, regardless of the health of an individual, if an individual's AChE activity falls below a certain percentage of normal, further exposure should be prevented.

The use of AChE measurements to signal the healthfulness of the work environment is well established and provides useful data concerning worker exposures to anticholinesterase agents (Lauwerys and Hoet, 1993). The abundant data on AChE activity permit the study of the relationship between clinical toxicity, AChE inhibition, and exposure. AChE measurements alone, however, are not sufficient to predict toxic thresholds. There are several factors that affect AChE inhibition.



Among these are the form of AChE affected (Sussman et al., 1991), route of administration of the inhibitor (Grob and Harvey, 1953), alterations in blood flow to target tissues (Maxwell et al., 1987), stereochemistry of the inhibitor (Benschop and de Jong, 1989), pharmacokinetics of the inhibitor (Reynolds et al., 1985), species (Martin, 1985), and health (Dillon and Ho, 1987). In general terms, the AChE status of a population can be used as an indicator of the magnitude and duration of exposure, but there is a need to augment enzyme-inhibition data with direct chemical measures of exposure to develop more protective health standards. In addition, any military field drinking-water standard must be more conservative than the standards applied in industry and agriculture because the nature of the chemicals and their potential use as chemical warfare agents is in direct contrast with the goals and objectives of a workplace hygiene program. For example, AChE monitoring in agriculture is designed to protect workers from excessive exposure and AChE monitoring in the military is designed to protect against impaired performance by personnel in a situation that might already be life-threatening.

#### FIELD DRINKING-WATER STANDARDS

McNamara et al. (1973) and McNamara and Leitnaker (1971) investigated the toxicity and fate of the chemical warfare agent VX. Variables considered in their model included the initial concentration, the removal rate, and the time to reach 50% concentration in the blood (effective biological half-life). Estimation of either the daily dose of an organophosphorus nerve agent or the accumulated effective dose is expressed as the percentage decrease in AChE activity.

Daniels (1990a) reviewed the removal rates and potencies of the organophosphorus nerve agents. The resulting interim maximum permissible concentrations (MPCs) for organophosphorus nerve agents in field drinking water were based on the relationship between AChE inhibition and toxicity. Table 3-1 contains Daniels's estimated MPCs for 50% inhibition as well as the subcommittee's MPCs for 25% inhibition for each of the four organophosphorus nerve agents. The concentrations were calculated on the basis of depression of red-blood-cell AChE not exceeding either 50% or 25% of normal red-blood-cell-AChE activity. The

d (Sussman et al., 1991), and Harvey, 1953), alteration et al., 1987), stereochemistry (1989), pharmacokinetics of (Martin, 1985), and health AChE status of a population and duration of exposure-inhibition data with direct more protective health standing-water standard must be in industry and agriculture for potential use as chemical goals and objectives of a AChE monitoring in agricultural exposure and AChE effect against impaired performance already be life-threatening.

## STANDARDS

and Leitnaker (1971) investigated warfare agent VX. Variables concentration, the removal in the blood (effective biologically dose of an organophosphorus dose is expressed as the

ates and potencies of the organophosphorus nerve agents in field between AChE inhibition estimated MPCs for 50% inhibition for each agents. The concentrations were blood-cell AChE not exceed blood-cell-AChE activity. The

**TABLE 3-1** Maximum Permissible Concentrations for Organophosphorus Nerve Agents<sup>a</sup>

Agent	Consumption Rate and Corresponding MPC, $\mu\text{g/L}$	
	5 L/day	15 L/day
AChE depression not > 50%		
VX	15.0	5.0
GD	12.0	4.0
GB	28.0	9.3
GA	140.0	46.0
AChE depression not > 25%		
VX	7.5	2.5
GD	6.0	2.0
GB	13.8	4.6
GA	70.0	22.5

<sup>a</sup>Assumes a 70-kg person consuming field drinking water at 5 L/day or 15 L/day for up to 7 days.

Sources: Daniels (1990a) and the subcommittee's estimate of 25% AChE inhibition.

MPCs assume a 70-kg person consuming field drinking water at 5 L/day or 15 L/day for up to 7 days.

The MPCs for 25% inhibition of AChE are advocated as standards at this time based on the limited dose-response data available and on the likelihood that AChE inhibitions adversely affecting performance are smaller than previously thought. Use of AChE to develop a standard results in an extremely conservative value; however, it is justified, given the need to protect health and assure against decreased battlefield performance.

Using available data, Saady (1991) computed equivalent dose estimates of the organophosphorus nerve agents that would be expected to be immediately dangerous to life or health (IDLH) via inhalation exposure in humans (Table 3-2). IDLH concentrations are defined as 30-min air concentrations that would produce such signs and symptoms as tight-

TABLE 3-2 Comparison of Estimated Doses and Proposed Field Drinking-Water Standards

Agent	30-Min IDLH Inhalation Dose, mg/m <sup>3</sup>	Estimated IDLH Oral Dose, μg/kg <sup>a</sup>	24-hr Water Dose, μg/kg <sup>b</sup>
VX	0.04	0.7	0.5
GD	0.06	1.1	0.4
GB	0.18	3.2	1.0
GA	0.18	3.2	5.0

<sup>a</sup>Minute volume (2.5 m<sup>3</sup>/hr) × time (0.5 hr) × IDLH (mg/m<sup>3</sup>)/70 kg.

<sup>b</sup>Drinking-water volume (L/day) × drinking-water concentration (μg/L)/70 kg.

Sources: Saady (1991) and subcommittee calculations.

ness of the chest, headache, runny nose, and miosis. For comparative purposes, inhalation exposures are considered more analogous to intravenous exposures than to ingestion or dermal contact (Somani, 1992). With respect to route and rate of exposure, absorption of organophosphorus nerve agents from the gastrointestinal tract is expected to be intermittent during waking hours. Thus, the extent of absorption from the gastrointestinal tract is considered to be substantially less than the extent of absorption following inhalation exposures (Grob and Harvey, 1953).

To compare the total body dose allowed by the 30-min IDLH to the total dose allowed by the proposed drinking-water standards for 1 day, the subcommittee converted both the air-concentration IDLH (in milligrams per cubic meter, Table 3-2) and the proposed drinking-water standard (in micrograms per liter, Table 3-1) to equivalent dose estimates in micrograms per kilogram. To convert the IDLH to dose equivalents, assume a moderate minute volume (2.5 m<sup>3</sup>/hr) for 30 min for a 70-kg person. Assuming that 100% of the inhaled chemical is retained and absorbed, the dose equivalent can be estimated; these values are provided in Table 3-2, column 3. Please note that in the absence of agent-specific data characterizing retention and absorption of the human lung, the subcommittee has made the protective default assumption of 100% retention and absorption for purposes of calculation. It is likely that some fraction < 100% is actually retained during inhalation exposure.

## s and Proposed Field

ed IDLH	24-hr Water
Dose,	Dose, $\mu\text{g}/\text{kg}^b$
	0.5
	0.4
	1.0
	5.0

$\times$  IDLH ( $\text{mg}/\text{m}^3$ )/70 kg.  
water concentration ( $\mu\text{g}/\text{L}$ )/70

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default assumption of 100%  
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luring inhalation exposure.

To change the corresponding proposed drinking-water standards to dose equivalents, the subcommittee used the proposed MPC at 25% AChE inhibition (Table 3-1) times the ingested water volume per day (either 5 or 15 L) for a 70-kg person. Assuming that 100% of the orally ingested chemical is absorbed, the dose equivalent can be estimated; these values are provided in Table 3-2, column 4.

The dose equivalent provided by the proposed drinking-water standard is less than the IDLH dose equivalent for VX, GD, and GB by 29%, 64%, and 69%, respectively (Table 3-2, columns 3 and 4). The proposed drinking-water-standard dose equivalent for GA is higher than the IDLH dose equivalent for two reasons. First, the IDLH estimate is conservative because GA and GB are considered to be equally toxic (Saady, 1991). Available data for GA are sparse. Chresthull (1957) reported the  $\text{LC}_{50}$  (the product of concentration and time that produces 50% mortality) of GA to be 71%, 63%, and 40% of the  $\text{LC}_{50}$  of GB in the mouse, rat, and monkey, respectively. Therefore, in the three animals studied, GA was found to be 29-60% less toxic than GB by inhalation. Comparable human data are not available. Second, Daniels (1990a) describes the estimated value for potency ( $k$ ) used in the pharmacokinetic model for GA ( $k_{\text{GA}} = 1$ ) to be 20% of the value for GB ( $k_{\text{GB}} = 5$ ). Based on the animal studies of Chresthull (1957), the subcommittee observed that the Daniels (1990a) assumed value for  $k_{\text{GA}}$  is low, resulting in an inflated MPC estimate for GA in water. Based on the work of Chresthull (1957), the subcommittee estimates that the  $k$  value for GA likely approximates 60% of the  $k$  value for GB (i.e.,  $k_{\text{GA}} = 3$ ). Because oral ingestion of GA is considered less toxic than inhalation of GA and because the assumed exposure time is 24 hr per day (for a maximum of 7 days), as opposed to 30 min for the IDLH exposure time, it is the subcommittee's view that the proposed field drinking-water standards for organophosphorus nerve agents (Table 3-1) are sufficiently protective.

## CONCLUSIONS AND RECOMMENDATIONS

It has been over 20 years since Hayes (1975) suggested that concurrent biomonitoring of AChE activity and urinary metabolites could yield a complimentary analysis of the status of persons exposed to organophosphorus chemicals. Measurements of AChE inhibition are indicative of

recent exposure experiences. Similarly, urinalysis would reveal day-to-day exposure experience because of the rapid clearance of metabolites in the urine. Until data similar to those called for by Hayes (1975) are developed for the organophosphorus nerve agents, the subcommittee recommends that guidelines for exposure to organophosphorus nerve agents in field drinking water be based on an estimated 25% inhibition of AChE. Hayes (1982) pointed out that the lower limit of statistical reliability in measuring changes in red-blood-cell-AChE activity is 20%; changes that are less than 20% cannot be detected reliably. As shown in Table 3-1, use of AChE to develop standards results in conservative interim standards. However, conservative standards might be justified since drinking-water standards are based on data obtained from human exposures (Daniels, 1990a) and are designed to protect the health and combat readiness of troops in the field.

The Army's proposed standards for organophosphorus nerve agents are based on 50% AChE inhibition. It proposed standards of 4  $\mu\text{g/L}$  and 12  $\mu\text{g/L}$  for a water consumption of 15 L/day and 5 L/day, respectively. The subcommittee, however, disagrees with the Army's approach of using 50% AChE inhibition as the basis for the standards. Clinical signs and symptoms of toxicity of organophosphorus nerve agents have been reported to occur in some individuals at 50% inhibition of AChE. In addition, a 50% inhibition of AChE might be associated with performance degradation in healthy adults. To accommodate for the biological variability inherent in red-blood-cell acetylcholine measurements (up to a 2-fold difference) and the possibility of confounding effects from exposure to other anticholinesterase chemicals, to assure against decreased battlefield performance, and to protect previously sensitized individuals, the subcommittee selected an AChE inhibition level of 25% as a definite NOAEL. It should be noted that the lowest level of statistical reliability in measuring AChE changes is approximately 20%; changes that are less than 20% cannot be detected reliably.

Based on the available data, the subcommittee recommends that the 25% AChE inhibition level be used as the basis for the field drinking-water guidelines for organophosphorus nerve agents and recommends the following guidelines for the organophosphorus nerve agents: GA, 22.5  $\mu\text{g/L}$  and 70.0  $\mu\text{g/L}$ ; GB, 4.6 and 13.8  $\mu\text{g/L}$ ; GD, 2.0 and 6.0  $\mu\text{g/L}$ ; and VX, 2.5 and 7.5  $\mu\text{g/L}$ —assuming a water consumption of 15

alysis would reveal day-to-clearance of metabolites in or by Hayes (1975) are dents, the subcommittee recognizes phosphorus nerve agents estimated 25% inhibition of lower limit of statistical reliability-AChE activity is 20%; cted reliably. As shown in s results in conservative in-standards might be justified data obtained from human d to protect the health and

nophosphorus nerve agents sed standards of 4  $\mu\text{g/L}$  and / and 5 L/day, respectively. h the Army's approach of e standards. Clinical signs rus nerve agents have been 1% inhibition of AChE. In be associated with perform-ommodate for the biological holine measurements (up to founding effects from expo-to assure against decreased ously sensitized individuals, n level of 25% as a definite level of statistical reliability / 20%; changes that are less

mittee recommends that the basis for the field drinking-ve agents and recommends sphorus nerve agents: GA, 3.8  $\mu\text{g/L}$ ; GD, 2.0 and 6.0 g a water consumption of 15

and 5 L/day, respectively. The subcommittee concludes that these guidelines are appropriate until the results of future research indicate that 25% AChE inhibition is inadequate or overly conservative. In addition, the subcommittee identifies the following research needs:

- **Dose-Response Relationship.** The use of AChE inhibition alone is not an adequate quantitative indicator of exposure to organophosphorus nerve agents. Daniels (1990a) reviewed the multiple factors affecting the measurement of AChE activity in animals and humans. Based on that review, only the most conservative field drinking-water standards are acceptable pending development of more dose-response data directly relating the toxicity of organophosphorus nerve agents to exposure. Extensive studies during the past 15 years with structurally related methyl and ethyl organophosphate insecticides have shown the corresponding dialkyl phosphates to be suitable biomarkers in 24-hr urine specimens. The biomarkers are stable and readily derivable to analytes, which can be measured in parts-per-billion amounts. The use of those biomarkers as indicators of exposure needs further investigation.

- **Evaluation of Model.** Daniels (1990a) noted that the calculated MPCs must be evaluated further. Supporting data are needed to (1) confirm the use of AChE activity as an indicator of the potential for an individual to develop adverse health effects, (2) ascertain the uncertainties about individual variability, and (3) confirm the use of butyryl cholinesterase recovery data both for indicating tissue recovery and for deriving permissible exposure levels. Those three factors should be evaluated using enzyme and chemical biomarkers (see "Dose-Response Relationship" above).

- **Medical Doctrine for Pretreatment.** The current military medical doctrine requires that military personnel with potential for exposure to organophosphorus nerve agents undergo treatment with pyridostigmine bromide both before and during a battlefield exposure (Dunn and Sidell, 1989; U.S. Army, 1990b). Pyridostigmine bromide is a carbamate that binds reversibly to AChE. It is administered prophylactically and is intended to preserve enough AChE to allow a person to survive exposure to organophosphorus nerve agents. The effectiveness of pyridostigmine bromide should be investigated further.

- **Performance Criteria.** It is recognized that the present set of

interim standards are conservative, and it is only speculative that they could represent the threshold above which significant impaired performance could occur (Daniels, 1990a). However, performance criteria for military personnel operating complicated equipment, including aircraft, weapons systems, and heavy machinery, are critical to the subcommittee's recommendation that field drinking-water guidelines based on 25% AChE inhibition be adopted for the entire class of organophosphorus nerve agents.

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# *Guidelines for Sulfur Mustard Agents*

## INTRODUCTION

**T**he various forms of sulfur mustard that have been used as chemical warfare agents are vesicants that produce blisters on exposed skin. They can damage the eyes as well as the respiratory and gastrointestinal tracts and are lethal at high doses. Sulfur mustard (bis(2-chloroethyl)sulfide,  $C_4H_8Cl_2S$ ) is a cellular poison, a mutagen, and a recognized human carcinogen (Saracci, 1981; NTP, 1989; BNA, 1990; IOM, 1993). Chemical and physical properties are more fully described in *Veterans at Risk* (IOM, 1993) and in the "Material Safety Data Sheets" prepared by the Edgewood Research Development and Engineering Center (ERDEC, 1990, 1992).

Modern chemical warfare agents might include any of the following three sulfur mustard formulations: Agent HD (distilled sulfur mustard), Agent THD (HD "thickened" with the addition of an acryloid copolymer to increase viscosity and, thus, persistence), and Agent HT (a plant-run mixture of about 60% HD and 40% T (bis-2-(2-chloroethylthioethyl)-ether,  $C_8H_{16}Cl_2OS_2$ ) and some impurities). The addition of T lowers the freezing point and expands the effective temperature range over which HT might be used in chemical warfare.

The literature on the toxicity of sulfur mustard agents primarily contains information on the toxicity of HD. The subcommittee assumed



that the toxicity of the other sulfur mustard agents—THD and HT—is similar to that of HD.

The field drinking-water standard for sulfur mustard that is used by the armed services (triseservices) is 200  $\mu\text{g/L}$  of water for periods of consumption that do not exceed 7 consecutive days (short-term consumption) (U.S. Army, 1986, 1990c). That standard assumes that field drinking water contains no other toxic materials. The proposed triservice standard, as documented in Dacre and Burrows (1988) and approved by the Tri-Service Steering Committee in 1991, is 140  $\mu\text{g/L}$  and 47  $\mu\text{g/L}$ , assuming a water consumption of 5 and 15 L/day, respectively. The standard was based on a no-observed-effect level (NOEL) of 100  $\mu\text{g/kg}$  in a 90-day exposure study of rats (Sasser et al., 1988a,b). The adverse effect observed was epithelial hyperplasia of the rat forestomach. It should be noted that field drinking-water disinfection (i.e., excess chlorination) can degrade sulfur mustard agents and might eliminate the threat of ingestion exposure; chlorine solutions are considered decontaminants for sulfur mustard agents (Sidell, 1992).

The Army Field Manual 10-52-1 (U.S. Army, 1991) indicates that HD is not considered a water contaminant because of its density and water insolubility and that blister agents (mustard and lewisite) are less of a threat than nerve agents because of their low solubility. These determinations are supported by physical and chemical characteristics known for sulfur mustard—i.e., that HD is sparingly soluble (0.68-0.92 g/L at 25°C) in water, and HT is considered practically insoluble; that sulfur mustard freezes at 13-15°C and might become a semisolid at temperatures near the freezing point (such as those found at the bottom of water pools); and that hydrolysis occurs slowly, forming a thin "monolayer," after which reaction rates for the entire volume of agent droplet or mass are negligible (Dacre and Burrows, 1988; Somani, 1992; IOM, 1993). The subcommittee agrees with observations made by Dacre and Burrows (1988) that any sulfur mustard agent in drinking water is most likely undissolved.

## TOXICITY

A review of the toxicity data on sulfur mustard agents reveals that

agents—THD and HT—is

er mustard that is used by  
water for periods of con-  
(short-term consumption)  
sumes that field drinking  
proposed triservice stan-  
1988) and approved by the  
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y, respectively. The stan-  
(NOEL) of 100  $\mu\text{g/kg}$  in a  
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there are no controlled oral studies in humans, thus necessitating extrapolation from animal data (Dacre and Burrows, 1988; Papirmeister et al., 1991; Watson and Griffin, 1992; IOM, 1993). Two recent gavage studies involving exposure of Sprague-Dawley rats to HD have been completed (Sasser et al., 1989a,b). These investigations provide data that can be used to support a determination of a field drinking-water standard for HD.

In one of the studies (Sasser et al., 1989a), HD dissolved in sesame oil was administered by gavage 5 days per week for 13 weeks to Sprague-Dawley rats. Doses administered were 0, 0.003, 0.01, 0.03, 0.1, and 0.3 mg/kg of body weight. The authors reported the following:

No dose-related mortality was observed. A significant decrease in body weight was observed in both sexes in the 0.3 mg/kg [300  $\mu\text{g/kg/day}$ ] dose group. . . . The only treatment-related lesion associated with the gavage exposure upon histological evaluation was epithelial hyperplasia of the forestomach of both sexes at 0.3 mg/kg. The forestomach of one 0.1 mg/kg male was also ulcerated. The hyperplastic change was minimal and was characterized by cellular disorganization of the basilar layer. . . . The estimated NOEL [no-observed-effect level] for HD in this 90-day study is 0.1 mg/kg/day when administered orally [Sasser et al., 1989a, p. 4].

The incidence of forestomach ulcers (1/24) in the exposed animals did not differ from that observed in the controls. However, the study does not state whether pair-feeding was performed. Thus, it is unclear whether the observed weight loss in rats is due to a toxic response or to reduced ingestion of food

The subcommittee concluded that the findings of Sasser et al. (1989a) and the analysis of Dacre and Burrows (1988, p.14) on the drinking-water criteria do not support consideration of 300  $\mu\text{g/kg/day}$  (0.3 mg/kg/day) as the acute lowest-observed-effect level (LOEL). The subcommittee concluded that the findings of Sasser et al. do support consideration of 100  $\mu\text{g/kg/day}$  (0.1 mg/kg/day) as the NOEL, as used in the analysis of Dacre and Burrows (1988). Note that the procedure used by Dacre and Burrows to estimate a NOEL from the data of a draft report of Sasser et al. (1989a) (i.e., LOEL/rating-effect value ( $RV_e$ )) is an unsubstantiated procedure and not endorsed by the U.S. Environmental Protection Agency (EPA). The  $RV_e$  is used to calculate composite scores for

determining reportable-quantity (RQ) estimates (EPA, 1984). NOEL and LOEL values are to be based on animal or human data from the literature.

Based on a NOEL of 100  $\mu\text{g/kg/day}$  (0.1 mg/kg/day) in rats and an uncertainty factor of 10 to account for interspecies differences, the calculated average allowable daily intake (ADI) in humans is  $100/10 = 10$   $\mu\text{g/kg/day}$ . No uncertainty factor for intraspecies differences in toxic response was applied because military personnel are assumed to be healthy. Therefore, the guidelines recommended by the subcommittee for sulfur mustard in field drinking water, assuming a water consumption of 5 and 15 L/day, are calculated as follows:

$$\begin{aligned} C_{dw} (5 \text{ L/day}) &= \frac{(10 \mu\text{g/kg/day})(70\text{-kg man})}{5 \text{ L/day}} \\ &= 140 \mu\text{g/L.} \\ C_{dw} (15 \text{ L/day}) &= 47 \mu\text{g/L.} \end{aligned}$$

The majority of the subcommittee recommends use of a single uncertainty factor of 10 for the following reasons:

1. The experimental NOEL identified from the study of Sasser et al. (1989a) was based on forestomach hyperplasia in rats. Humans have no organ comparable to the rat forestomach, so the relevance of these rat data to humans is debatable. Also, the use of sesame oil as a carrier likely enhanced the potential for cellular damage from exposure to sulfur mustard agents because sulfur mustard is freely soluble in oils and fats.
2. The acute toxic effects observed in rats are not considered to be those that would incapacitate military personnel during a short (7 days) exposure.

A companion two-generation reproductive study of HD was performed in the same laboratory in 1989 (Sasser et al., 1989b). In this study, Sprague-Dawley rats were administered HD by gavage at doses of 0, 0.03, 0.1, 0.4 mg/kg before mating and throughout gestation, parturition, and lactation for 42 weeks. "No adverse effect on reproductive performance, fertility or reproductive organ weights of male or female rats" was observed (Sasser et al., 1989b). At the highest dose,

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growth of  $F_1$  rats of both sexes was reduced, and the growth of  $F_1$  and  $F_2$  offspring was depressed during lactation. A dose-related lesion of the forestomach squamous epithelial mucosa was observed in both sexes. The investigators concluded that the NOEL "in this study was  $<0.03$  mg/kg for toxicity and  $>0.4$  mg/kg for reproductive effects" (Sasser et al., 1989b).

An additional ingestion study considered by the subcommittee is the dose-range study performed by Hackett et al. (1987a); the NOEL identified from this study was 0.2 mg/kg/day. However, the small sample size and single-gender (pregnant females) population precluded its use in the present analysis.

### CANCER-RISK ESTIMATE

Sulfur mustard is a classic alkylating agent and readily reacts with components of DNA, RNA, and proteins. These characteristics make sulfur mustard a potent cell poison that is particularly toxic to mitotic cells; cytostasis, mutation, and cell death can also occur. A number of cell systems exhibit chromosomal aberrations following experimental exposure to sulfur mustard. In addition, mutagenic responses have been observed in *Drosophila*, mouse lymphoma cells, *Neurospora crassa*, and *Salmonella*. The cytogenetic and mutagenic response of sulfur mustard exposure is considered similar to that of x-rays (Watson et al., 1989; Watson and Griffin, 1992; IOM, 1993).

Retrospective studies of military veterans exposed to battlefield concentrations of sulfur mustard during World War I as well as British and Japanese chemical-weapons factory workers exposed during production of sulfur mustard and sulfur mustard munitions during World War II have been sufficiently compelling to have sulfur mustard classified as a Class 1 human carcinogen by the International Agency for Research on Cancer (IARC) (Saracci, 1981; Watson et al., 1989; IOM, 1993). Malignancies were found primarily in the upper respiratory tracts of humans after inhalation exposure. Thus, animal and human data are considered sufficient to support a casual relationship between exposure to sulfur mustard and subsequent cancer induction in humans.

By deriving an ingestion dose-response slope  $Q^*$ , by the procedure

outlined by Watson et al. (1989, 1992) ( $Q^*_{HD} = 14.95 [(mg/kg)/day]^{-1}$ ), an estimate of lifetime cancer risk at the proposed and recommended ingestion guidelines can be calculated. Estimates are presented with adjustment for a single 7-day exposure in a lifetime (70 years) (i.e.,  $2.7 \times 10^{-4}$ ) and  $Risk = (Q^*)(D)$ , where Risk is the additional lifetime risk of developing cancer from ingestion of field drinking water containing sulfur mustard agents,  $Q^*$  is the risk per milligrams per kilograms per day and  $D$  is the dose (Anderson and the Carcinogen Assessment Group, 1983).

For a total intake of  $700 \mu g/kg/day$  for 7 days ( $140 \mu g/L \times 5 L/day$ ), the estimated cancer risk is  $4.1 \times 10^{-5}$ . However, because of the limited water solubility of HD, the actual dose might be much less than computed, making this cancer-risk estimate too high. The Code of Maryland Regulations (Title 26.11.15, Part .01 A(8)) (BNA, 1990) has defined an acceptable cancer risk for inhalation exposure to sulfur mustard as "not more than 1 in 100,000 ( $1 \times 10^{-5}$ ).\" Exposures that generate lifetime cancer risks less than  $10^{-6}$  are rarely regulated by EPA or the Food and Drug Administration. Consumption of drinking water containing sulfur mustard agents at the concentrations proposed here theoretically carries a potential increased lifetime risk of cancer on the order of  $10^{-5}$ .

Field commanders and their troops need to be aware of the potential for increased lifetime risk of developing malignancy from exposure to sulfur mustard agents, as well as the magnitude of that potential risk. However, no acute effects (nausea, gastrointestinal upset, etc.) are expected to occur following consumption (for a period of 7 days or less) of field drinking water contaminated with sulfur mustard agents at or below the concentrations proposed here.

### EXTRAPOLATION DIFFICULTIES

In the studies described above, rats exposed to sulfur mustard exhibited forestomach ulceration or hyperplasia. Since humans do not have an organ that is homologous to the rat forestomach, there is some debate as to the relevance of these lesions in estimating potential adverse health effects in humans exposed to sulfur mustard agents.

Other animal-to-human extrapolation difficulties stem from the nature

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of the vehicle used to administer sulfur mustard agents to the rats and the route of exposure. The use of sesame oil as a carrier for a lipid-soluble compound, such as sulfur mustard, artificially enhances the potential for cellular damage in tissues (e.g., rat forestomach) coming in contact with the mustard-sesame oil solution. With respect to the route of exposure, the agent was administered by gavage, resulting in portal entry effects, not systemic effects. The gavage route of exposure is not directly comparable to drinking-water ingestion in humans.

Based on these extrapolation difficulties, it can be assumed that any estimates of field drinking-water guidelines derived from these data will result in conservative estimates considered protective for humans.

## CONCLUSIONS AND RECOMMENDATIONS

The field drinking-water guidelines for sulfur mustard recommended by the subcommittee are 140 µg/L and 47 µg/L, assuming a water consumption of 5 L/day and 15 L/day, respectively. Those guidelines represent a 30% reduction from the existing short-term standard of 200 µg/L for 5 L/day water consumption.

Field commanders and their troops should understand the following with respect to the proposed guidelines:

- Providing that no other toxic compounds are present in the water supply, acute effects (e.g., nausea or gastrointestinal upset) are not expected to occur following consumption of field drinking water at the recommended guideline concentrations.
- These field drinking-water guidelines are based on extrapolations from limited studies in laboratory animals administered sulfur mustard by gavage.
- Sulfur mustard is a known human carcinogen. Consumption of drinking water containing sulfur mustard for 7 days at guideline concentrations theoretically increases the lifetime risk of developing cancer by approximately  $10^{-5}$ . This risk should be weighed against the soldiers' daily needs for adequate hydration.
- It is not known the extent to which chlorination or iodination will degrade sulfur mustard present at various concentrations in field drinking

water. It is possible that current military training and disinfectant<sup>1</sup> materials that are used for field drinking-water treatment will substantially reduce concentrations of sulfur mustard in water. It is recommended that this approach for mitigating exposure to sulfur mustard agents be investigated further.

- Some available data characterize the efficacy of a new technique for removing HD from experimental waters. This technique involves a purification tablet that would replace the Globaline iodine tablet now in use (fielded since 1952) (Geomet, 1991; Powers, 1993). Use of the new water-purification tablets (Chlor-Floc) enhanced mustard agent degradation in EPA No. 2 standard water by approximately 10% at 5°C and by approximately 30% at 10°C (Geomet, 1991; Powers, 1993). Unfortunately, these investigations do not provide a comparison of degradation of HD in experimental waters treated with the new tablets and degradation of HD in waters treated with the currently used iodine tablets or excess chlorination. The subcommittee recommends that such studies be conducted.

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<sup>1</sup>"Any oxidant, including but not limited to chlorine, chlorine dioxide, chloramines and ozone added to water in any part of the treatment or distribution process, that is intended to kill or inactivate pathogenic organisms" (U.S. Army, 1991, p. G-3). Military doctrine and guidance for disinfectant use are provided in Field Manuals 10-52 and 10-52-1 (U.S. Army, 1990c, 1991).

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efficacy of a new technique. This technique involves a saline iodine tablet now in use (Powers, 1993). Use of the new iodine mustard agent degrades approximately 10% at 5°C and by Powers, 1993). Unfortunately, a comparison of degradation of new tablets and degrading old tablets used iodine tablets or recommends that such studies be

rine, chlorine dioxide, chloramine, and other disinfectants for the treatment or distribution of pathogenic organisms" (U.S. Army, 1990c, 1991).

## 5

# Guidelines for T-2 Toxin

## INTRODUCTION

**T**-2 toxin is a mycotoxin, a compound that belongs to the trichothecene class. It is formed as a secondary metabolite by some species of *Fusarium* molds. The oral LD<sub>50</sub> of T-2 toxin in animals ranges from 3 to 5 mg/kg, and the dose-response curve is very steep. Because of the lipophilic nature of trichothecenes, they are rapidly and completely absorbed from the gastrointestinal tract and quickly distributed to all major organs. The mechanism by which T-2 toxin causes cell death is through the inhibition of protein synthesis at the 80S ribosome. T-2 toxin is strongly emetic at doses of 0.1-1 mg/kg of body weight in some animal species (such as swine and monkeys), making it difficult to estimate LD<sub>50</sub>s accurately in these species. The mechanism of action of emesis is not known.

Although T-2 toxin has been implicated as a chemical warfare (CW) agent in Southeast Asia and Afghanistan, no accurate human-exposure data are available. T-2 toxin purportedly was dispersed aerially as a CW agent in combat zones in Southeast Asia and Afghanistan, where inhabitants described the yellow substance as "granules or mists that fell like rain"; this substance later became known as "yellow rain" (Haig, 1982; NRC, 1983). T-2 toxin was claimed to be the lethal ingredient in "yellow rain" that was dispersed in Laos and Kampuchea in 1981 and to



appear as yellow spots on some rocks and leaves and in water samples taken from locations near battlefields.

Although there is little reliable information on the adverse health effects of T-2 toxins in humans, the most common toxic effect is thought to be nausea and vomiting. This finding is based on the considerable data compiled on the toxicology of another structurally similar trichothecene mycotoxin, diacetoxyscirpenol (DAS). DAS was used as an experimental antineoplastic drug in the late 1970s. The LD<sub>50</sub> values and emetic dose for DAS in laboratory animals are similar to those for T-2 toxin. DAS was used in several Phase I and Phase II clinical trials for the treatment of cancer patients who had not responded to approved therapies. According to these studies, nausea and vomiting were the most common side effects of treatment. Other effects included hypotension, CNS disturbances, diarrhea, headaches, fever, and chills. Myelosuppression was also observed with prolonged exposure. Some of these effects were observed at doses as low as 0.2 mg/m<sup>2</sup> (NRC, 1983). Based on toxic episodes related to *Fusarium*-contaminated grain products, there is circumstantial evidence linking T-2 toxin to alimentary toxic aleukia (ALA). In outbreaks such as these, there is usually more than one mycotoxin involved, so it is difficult to determine the contribution of T-2 toxin alone to the etiology of ALA (NRC, 1983). The use of the data from the clinical trials is limited because the trials involved a small number of people with an existing disease (i.e., cancer).

The Army conducted experiments to study the toxicity of T-2 toxin in monkeys (Wannemacher et al., 1991). The experiment included LD<sub>50</sub> studies via the intravenous and dermal routes as well as pharmacokinetic studies. The results of the LD<sub>50</sub> studies showed that the toxic effects of T-2 toxin are similar to the chemotherapeutic drug DAS. Both T-2 toxin and DAS produce severe gastrointestinal toxic effects, such as diarrhea and vomiting. The pharmacokinetic studies in monkeys identified metabolites of T-2 toxin; the T-2 metabolites can be used to identify T-2-exposed persons.

#### FIELD DRINKING-WATER STANDARDS

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26 µg/L and 8.7 µg/L, assuming a water consumption of 5 L/day and 15 L/day, respectively (Daniels, 1990b). These values are based on data derived from Phase I and Phase II clinical trials in which DAS was administered to cancer patients. Toxicological studies in animals indicate that T-2 toxin and DAS are approximately equally potent. Therefore, the use of DAS dose-response data was considered appropriate when estimating the toxicity of T-2 toxin in humans.

To determine the concentrations of CW agents in field drinking water, a 7-day exposure and a water consumption of either 5 L/day or 15 L/day for arid climates were assumed. Based on a consideration of the circumstances under which these water standards would be invoked (war time) and the population that would be exposed (presumably healthy soldiers), the use of conservative safety factors, such as those used for setting standards affecting general populations, was deemed inappropriate. Specifically, safety factors were not used when deriving the concentrations for the proposed guidelines because of the following:

- The acceptable concentrations of T-2 toxin in water were based on data from 5-day clinical trials in which DAS, an equipotent structural analog, was administered to patients with cancer. Patients with cancer are assumed to represent a more sensitive population, due to their disease and age, in comparison to a military population. The major performance-limiting effect that a soldier would exhibit following exposure to T-2 toxin would be nausea and emesis. It is not clear that the performance decrement caused by nausea and emesis in soldiers would be as incapacitating as nausea and emesis in patients who are already weakened by advanced disease and side-effects from previous exposure to chemotherapeutic agents.

- Given that T-2 toxin and DAS are strongly emetic at doses approximately one-tenth the LD<sub>50</sub>, the highest dose of DAS observed not to cause nausea and emesis in the 5-day clinical trials was identified as the NOEL (Murphy et al., 1978). That NOEL was then adjusted to account for an exposure period of 7 days.

- In the clinical trials, DAS was administered to patients by rapid intravenous (i.v.) infusion. An increase in the time of total-dose administration led to an increase in the tolerated dose (Goodwin et al., 1978). Therefore, it is reasonable to assume that the peak blood concentration

of T-2 toxin expected from drinking water would be below the concentration achieved by rapid i.v. infusion. However, it should be borne in mind that an i.v. dose is not necessarily more potent at causing nausea and emesis than an oral dose (Goodwin et al., 1978). In fact, the opposite might be true if the toxin acts directly on the stomach. In support of that possibility, Goodwin et al. (1978) reported a 5- to 6-fold increase in the potency of oral versus i.v. administration in swine and monkeys given a minimum emetic dose of T-2 toxin.

Thus, these three extrapolations or approximations (cancer patients to soldiers; 5-day exposure adjusted for 7-day exposure; and exposure by i.v. administration vs. gavage) might together provide a small margin of safety for battlefield exposures. In fact, the proposed concentration is comparable to values extrapolated from animal data in which an emetic dose was administered in a long-term feeding trial and adjusted using a 10- and 100-fold safety factor.

Data from two of several clinical trials (Goodwin et al., 1978; Murphy et al., 1978) in which DAS was administered to patients with cancer were used to compute the acceptable exposure concentrations. Data from four other clinical studies were also examined (Diggs et al., 1978; Yap et al., 1979; Thigpen et al., 1981; Bukowski et al., 1982). This comprehensive analysis supported the Army's proposed standards for field drinking water. Short of a study in which humans are exposed to T-2 toxin or a study in which doses of CW agents used in combat are accurately reconstructed, the available data appear to be adequate. Figure 5-1 shows a summary of the data used to develop the standards.

The current field test kit for detecting T-2 toxin in water has a detection limit of 470  $\mu\text{g/L}$ . That limit is not useful when a standard of 8.7-26  $\mu\text{g/L}$  is being proposed. The subcommittee recommends that a field-test kit capable of detecting T-2 toxin at or below the concentrations of the proposed standards be developed and made available to soldiers.

## CONCLUSIONS AND RECOMMENDATIONS

The subcommittee concludes that the Army's extrapolations or approximations concerning exposure and toxicity are reasonable, appropri-

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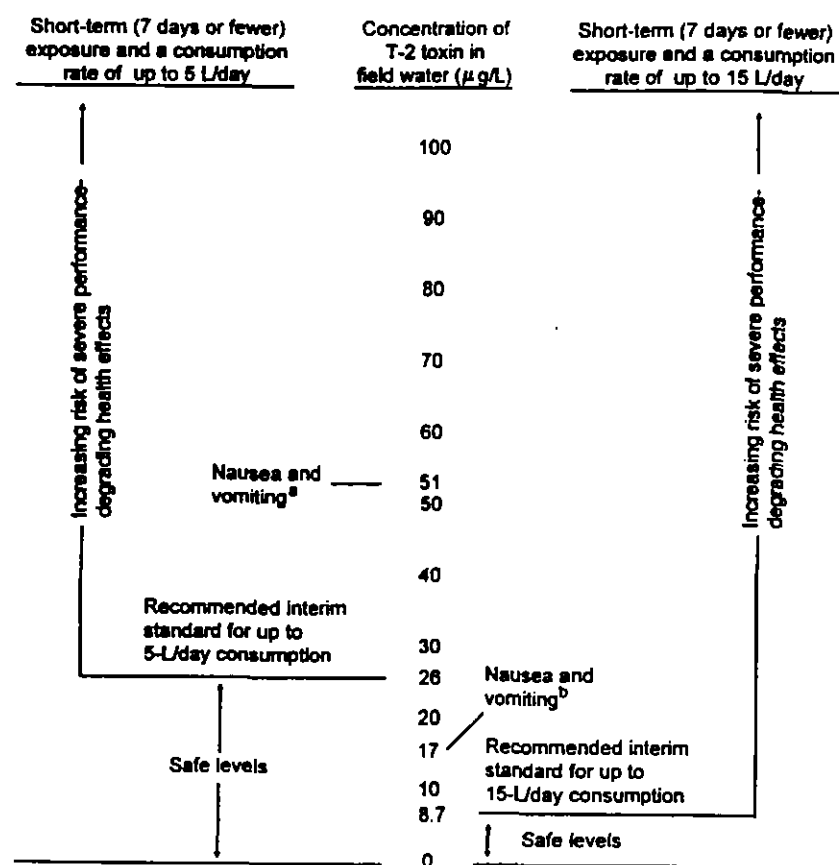
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**FIGURE 5-1** Health-effects summary for T-2 toxin in field drinking water (based on administration of DAS in clinical trials to cancer patients).

<sup>a</sup>Potentially performance-degrading health effects might include nausea, vomiting, diarrhea, generalized burning erythema, and mental confusion according to studies of DAS in clinical trials.

<sup>b</sup>Based on the lowest daily i.v. dose of DAS reported by Goodwin et al. (1978) to produce nausea and vomiting in cancer patients. Most severe health effects, including gastrointestinal problems, were reported in cancer patients administered a daily dose of DAS by rapid i.v. infusion for 5 days, a dose about 30 times greater than that used to calculate the standards. Therefore, concentrations of T-2 toxin that are 30 times greater than the recommended interim field drinking-water standards are expected to produce the most severe toxic symptoms.

Source: Daniels, 1990b.

ate, and conservative. The similarity in results obtained from the DAS clinical trials and the animal-data extrapolations provides some confidence in the appropriateness of the proposed field drinking-water standards of 26  $\mu\text{g/L}$  for 5 L/day water consumption and 8.7  $\mu\text{g/L}$  for 15 L/day water consumption. The subcommittee concludes that the Army's proposed field drinking-water standards for T-2 toxin are appropriate. Thus, the field drinking-water guidelines recommended by the subcommittee are the same as the Army's proposed standards.

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# 6

## *Guidelines for Lewisite*

### INTRODUCTION

**L**ewisite is an outdated and ineffective organoarsenical chemical warfare agent. However, it might still be encountered in battle-field situations. The formulation of lewisite (chlorovinylchloroarsine) as a war gas was done by W. Lee Lewis in 1918. It was considered an alternative to sulfur mustard, which had become the main chemical warfare agent in use by the end of World War I. Lewisite was used by the Japanese army during the Manchurian campaigns of the late 1930s and the early 1940s.

Lewisite is a potent blister agent. Like other blister agents, it not only produces casualties but also restricts use of terrain, hampers troop movements, and requires cumbersome protective gear (Somani, 1992). It is a colorless, oily liquid at room temperature with a faint "geranium-like" odor. It is more volatile than sulfur mustard and, therefore, can be used as a vapor over greater distances. To achieve greater effectiveness in combat, lewisite has been mixed with sulfur mustard. Because of its freezing point, lewisite is effective over a wider temperature range than sulfur mustard. Lewisite dissolves very slowly in water. The dissolved lewisite hydrolyzes rapidly to hydrochloric acid and lewisite oxide. It can form a surface film and globules that fall to the bottom of the water layer (Daniels, 1990c).

**TOXICITY AND MECHANISM OF ACTION**

Lewisite causes painful blistering of the skin and eyes. If decontamination does not occur within 1 min, lewisite produces severe damage to the cornea, and permanent loss of sight can result. Reddening of the skin begins within 30 min, and blistering appears about 13 hr after exposure. As a vesicant, lewisite is about four times as fast-acting as mustard and is much less persistent (Somani, 1992). Lewisite's effects are similar to those of sulfur mustard's, except that it is absorbed through the skin and acts as a systemic poison. Exposure to lewisite leads to pulmonary edema, diarrhea, restlessness, weakness, subnormal temperature, and low blood pressure. Prolonged exposure leads to severe pain in the throat and chest (U.S. Army and U.S. Air Force, 1975).

Trivalent arsenic is considered the component of lewisite that is primarily responsible for its vesicant and systemic toxicity; thus, field drinking-water standards for lewisite are expressed in terms of the arsenic fraction. In addition, the water-quality test currently used by the military does not detect lewisite directly; instead it detects the arsenic component.

Trivalent arsenic exerts its toxic effect by binding to sulfhydryl-containing proteins, especially enzymes, thus inhibiting pyruvate oxidation—a critical step in carbohydrate metabolism. The inhibition kills cells. The lipid solubility of lewisite also contributes to its toxic effects; trivalent arsenic readily penetrates skin, exerting its toxic action systemically and causing painful localized blistering. As a systemic toxicant, lewisite produces pulmonary edema, diarrhea, restlessness, weakness, subnormal temperature, and low blood pressure. Vascular damage, induced by lewisite, is partly responsible for effects such as blistering, tissue perforation, and hemorrhaging. Edema and hemorrhaging associated with lewisite exposure can lead to shock and death.

Human data concerning the toxicity of lewisite via the oral route of exposure are not available. However, there are limited toxicity data on lewisite ingestion from three animal studies.

In animals, ingestion of lewisite can produce acute inflammation of the mucous membrane of the stomach or intestine, which is characterized by hemorrhage, necrosis of epithelium, and submucous edema. Developmental effects have been reported in pregnant rats and rabbits exposed

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skin and eyes. If decontaminated, it produces severe damage to the skin as a result. Reddening of the skin appears about 13 hr after exposure and is as fast-acting as mustard.

Lewisite's effects are similar to those of mustard if it is absorbed through the skin. Exposure to lewisite leads to pulmonary edema, subnormal temperature, and severe pain in the chest (Force, 1975).

The most important component of lewisite that is primarily responsible for its systemic toxicity; thus, field tests expressed in terms of the arsenic test currently used by the military instead it detects the arsenic

by binding to sulfhydryl-containing enzymes, inhibiting pyruvate oxidation—the inhibition kills cells. The inhibition of pyruvate oxidation leads to its toxic effects; trivalent arsenic acts as a systemic toxicant, lewisite produces weakness, subnormal body temperature, and skin damage, induced by lewisite as blistering, tissue perforation, and hemorrhaging associated with lewisite.

Lewisite via the oral route of exposure has limited toxicity data on

produce acute inflammation of the respiratory tract, which is characterized by submucous edema. Development of pulmonary edema in rats and rabbits exposed

to lewisite by intragastric intubation. Rats were exposed for 10 days (on days 6-15 of gestation), and rabbits were exposed for 14 days (on days 6-19 of gestation). A no-observed-adverse-effect level (NOAEL) of 0.016 mg/kg/day in rabbits and 1.5 mg/kg/day in rats was identified (Hackett et al., 1987b). The NOAEL of 0.016 mg/kg/day in rabbits was selected for developing the proposed field drinking-water standards for lewisite.

There are no data on chronic toxicity resulting from the ingestion of lewisite.

Lewisite, as an arsenical, might be carcinogenic, although no specific studies were found in which the carcinogenicity of lewisite was evaluated. There is evidence that arsenic might act as a cocarcinogen and promote the carcinogenic process. It is capable of producing DNA damage; however, direct tests of its mutagenic potential have been inconclusive.

The effectiveness of lewisite as a chemical warfare agent depends in large degree on whether toxic doses can be produced in the battlefield. Field experiences indicate that doses large enough to affect military operations are probably not attainable with any reasonable expenditure of munitions (Gates et al., 1946). Neither saturation of fields nor delivery of thickened lewisite vapors through bomb and airplane spray has proved to be effective. This lack of sufficient exposure to lewisite might also account for the dearth of epidemiological data on the health effects of lewisite, although the literature on the toxic effects of arsenic in humans is abundant. Given the limited epidemiological data, the proposed drinking-water standards for lewisite (Daniels, 1990c) were derived from three animal studies—a sparse data base.

The shortcomings of those animal studies for predicting the effects in humans exposed to lewisite in water, and, in particular, in military personnel exposed to field drinking water, have been clearly recognized (Daniels, 1990c). For example, the obvious advantages that experimental studies offer, such as the ability to control genetics and diet and the opportunities for more intensive observations, are counterbalanced by the uncertainties of interspecies extrapolation. Therefore, biologically plausible assumptions, including best quantitative estimates, have been used to arrive at the proposed standards. In addition, the animal studies were evaluated in light of all relevant data on the health effects in question, the host, and the chemical itself. However, there are major data



gaps on the toxicity of lewisite, and the usefulness of most of the studies is limited by the lack of a satisfactory animal model. Little information exists on the reaction of lewisite with biologically important molecules, although it is reasonable to assume that, as with sulfur mustard, DNA is a major target (IOM, 1993).

There are no adequate data on the acute effects of lewisite following dermal exposure. Very little is known about its specific effects on skin, and data on its absorption, disposition, and excretion following dermal exposure are minimal. Microscopic examination of affected skin has not been pursued extensively.

The proposed Army standards for exposure to lewisite in field drinking water were derived from a rabbit study, in which the NOAEL was estimated to be 0.016 mg/kg/day (Hackett et al., 1987b). Converting the arsenic fraction of 0.0058 mg/kg/day to total consumption per day for a 70-kg human consuming 5 L or 15 L of water per day gives  $(0.0058 \times 70)/(5 \text{ or } 15 \text{ L}) = 0.08 \text{ and } 0.027 \text{ mg/L}$ , respectively. No additional safety factors were assumed. Whether the rabbit is the species most sensitive to lewisite is not known, and the applicability of the rabbit data to the human situation requires further evaluation. It is recommended that future consideration should include a comparative analysis of pharmacokinetics, metabolism, repair mechanisms, and genetic constitutions.

Neurological effects following acute exposure to lewisite have not been documented in animals. Acute exposure to high concentrations of lewisite leads to a shock syndrome that is thought to result from increased capillary permeability (Goldman and Dacre, 1989). No direct evidence exists that lewisite might cause neurological problems in humans, although arsenic is considered a neurotoxin and peripheral neuropathy has been reported in humans following a single arsenic exposure (Le Quesne and McLeod, 1977).

## CONCLUSIONS AND RECOMMENDATIONS

Given the limited data on the acute health effects associated with exposure to lewisite through ingestion of water by animals and humans, the subcommittee concludes that the Army's proposed interim standards for lewisite in military field drinking water are sufficient to reduce the risk of lewisite-induced health effects or performance degradation.

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## RECOMMENDATIONS

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The Army's proposed short-term drinking-water standards for lewisite are 220 and 75  $\mu\text{g/L}$  (or 80 and 27  $\mu\text{g/L}$  if expressed as the arsenic fraction), assuming a water consumption of 5 L/day and 15 L/day, respectively. Those standards represent an approximate 10-fold reduction from the previous drinking-water standard for lewisite of 2 mg/L (for 5 L/day consumption). It is further recommended that accompanying guidance for unit commanders underscores the following points:

- No human data are available on the health effects of lewisite following ingestion.
- These drinking-water guidelines are based on extrapolations from limited animal studies.
- Providing no other toxic compounds are present, acute effects are not expected at the assumed levels of water consumption.
- Some evidence suggests that lewisite might be carcinogenic (CDC, 1988); as a consequence, there might be some risk of developing malignancy later in life following lewisite exposure at the guideline levels.

At present, there are no field drinking-water monitoring capabilities that can reliably detect lewisite or elemental arsenic at the recommended concentrations. Therefore, the subcommittee recommends that field monitoring techniques be developed for detecting low concentrations of arsenic and lewisite.

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## *Guidelines for Cyanide*

### INTRODUCTION

**H**ydrogen cyanide has been known as a potent toxicant for over 200 years. It was used as a chemical warfare agent during World War I by France. Although it is highly volatile (and was later considered "militarily useless" because of its volatility), no deaths from its military use during World War I were ever reported (Haber, 1986). There are also reports of hydrogen cyanide being used as a war gas during the Iran-Iraq war in the 1980s (Lang et al., 1986; Heylin, 1988). However, because hydrogen cyanide can be detoxified rapidly by humans and because it is very volatile, massive amounts of the gas are needed for it to be effective as a chemical warfare agent.

Cyanide is primarily an environmental contaminant of industrial processes and usually enters the drinking water as industrial waste. It is used in the metal-processing industry for electroplating, heat treating, and metal polishing (California State Water Resources Control Board, 1963; Jenks, 1979) and can be found in waste waters from many mining operations that use cyanide compounds in the extraction of metals, such as gold and silver, from ore (Towill et al., 1978; Jenks, 1979). Microbial metabolism of nitrogenous compounds can also be responsible for the presence of cyanide in water (Knowles, 1976; Leduc, 1981).

Among the various chemicals that contain the cyanide moiety and that

can be found in water, hydrogen cyanide is the form that is of the most toxicological consequence (Scofield et al., 1988). Chlorination of water containing hydrogen cyanide results in the formation of cyanogen chloride, which is highly toxic but not as toxic as hydrogen cyanide (Cotton and Wilkinson, 1980), and other less toxic cyanates (California State Water Resources Control Board, 1963). Cyanogen chloride has limited solubility in water, persists for more than 24 hr, and slowly hydrolyzes to the cyanate ion. All cyanates are able to persist in aerobic water at pH 7 at 20°C for 10 days (Resnick et al., 1958).

### TOXICITY

The acute toxicity of cyanide has been well documented in humans and experimental animals. Symptoms of toxicity in humans include headache, breathlessness, weakness, palpitations, nausea, giddiness, and tremors (Gupta et al., 1979). Death results from respiratory arrest (Smith, 1980). Chronic exposure to cyanide can result in neuropathies, goiter, and diabetes (Hardy et al., 1950; El Ghawabi et al., 1975). The mode of action that leads to cyanide toxicity is to block electron transport, thus inhibiting enzymes in the cytochrome oxidase chain and, in turn, blocking oxygen use in metabolizing cells. That action can be rapidly lethal at high doses.

Blood cyanide concentrations are correlated with various health effects. The most reliable data are the measurements of cyanide concentrations in blood drawn from patients who received infusions of sodium nitroprusside (a cyanide-releasing drug) during surgery.

Table 7-1 lists the whole-blood cyanide concentrations at which health effects occur in animals and humans.<sup>1</sup> In the table, the first six entries are examples of "background" concentrations of cyanide measured in healthy people. They show that a measurable concentration of cyanide is normally present in human blood. The concentrations reported by Symington et al. (1978) are mean values; individual values range up to 0.32

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<sup>1</sup>The remainder of this section is a slightly modified excerpt from the Lawrence Livermore National Laboratory's report to the Army (Scofield et al., 1988).

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**TABLE 7-1 Whole-Blood Cyanide Concentrations and Health Effects**

Cyanide Conc., mg/L	Population	Health Effect	References
	Background level:		
<0.086	Nonsmoker	None	Chandra et al., 1980
<0.094	Smoker	None	
	Background level:		
0.016	Nonsmoker	None	Ballantyne, 1977
0.041	Smoker	None	
	Background level:		
0.08	Nonsmoker	None	Symington et al., 1978
0.18	Smoker	None	
	Occupational level:		
0.18	Nonsmoker	Complaints <sup>a</sup>	Chandra et al., 1980;
0.56 (0.23) <sup>b</sup>	Smoker	Complaints <sup>a</sup>	Gupta et al., 1979
0.20	Humans	Suggests toxic reaction	Berlin, 1977
0.22	SNP <sup>c</sup> -treated humans	None	Pasch et al., 1983
0.51	SNP-treated humans	Threshold for metabolic effects	Aitken et al., 1977; Schulz et al., 1982
0.90	SNP-treated humans	Metabolic acidosis	Aitken et al., 1977
1.0-10.0	Human poisonings	Toxicity and lethality	Niyogi, 1973
1.82 <sup>d</sup>	Mice	Lethal	Smith and Kruszyna, 1974
2.00	Dogs	No effects	Michenfelder and Tinker, 1977
2.9-28.7	Humans	Lethal	Bogusz et al., 1979
7.0-10.0	Dogs	Lethal	Michenfelder and Tinker, 1977

<sup>a</sup>Headache, weakness, palpitation, nausea, breathlessness, and tremors.

<sup>b</sup>Mean concentration if the highest concentration measured for one of eight subjects (2.2 mg/L) is not included.

<sup>c</sup>SNP, sodium nitroprusside.

<sup>d</sup>Blood concentration after a lethal dose (intraperitoneal administration); represents 50% of a population of laboratory mice.

Source: Schofield et al., 1988.

mg/L of whole blood for nonsmokers and 0.52 mg/L for smokers. These values are much higher than the concentrations reported by Chandra et al. (1980) and Ballantyne (1977). The variation might be due to the use of a different analytical method, or it might be due to the long interval between the time the blood samples were taken and the time the samples were analyzed. The storage conditions for the blood samples in the study by Symington et al. (1978) can result in cyanide formation. Workers exposed to cyanide gas and alkali cyanide salts via inhalation had mean blood cyanide concentrations of about 0.23 mg/L (Chandra et al., 1980). The high mean value (i.e., 0.56 mg/L) for smokers is primarily due to one very high value (2.2 mg/L); if that one value is excluded, the mean is 0.23 mg/L. Symptoms and signs reported for the workers include headache, palpitation, nausea, breathlessness, weakness, dizziness, and tremors—typical symptoms of cyanide poisoning (Gupta et al., 1979). According to the authors, those symptoms and signs were probably due to elevated inhalation exposures and associated high blood cyanide concentrations. Therefore, mean blood cyanide concentrations are not necessarily indicative of toxicity. Other symptoms noted for the workers—including pain and irritation in the throat and eyes—are attributable to the irritating properties of the alkali cyanide salt aerosols rather than to cyanide itself (NIOSH, 1976).

Berlin (1977) found that whole-blood cyanide concentrations above 0.2 mg/L might cause cyanide intoxication in humans. In measurements of cyanide concentrations in patients administered sodium nitroprusside, Pasch et al. (1983) determined that a whole-blood cyanide concentration of 0.22 mg/L would be safe for patients. Metabolic effects were not detected until about 1 mg/L. For example, Aitken et al. (1977) detected metabolic disturbances in patients administered sodium nitroprusside when whole-blood cyanide concentrations were above 0.9 mg/L. The threshold cyanide concentration was found to be 0.51 mg/L of whole blood. Pasch et al. (1983) indicated that cyanide concentrations above 2.2 mg/L of whole blood in patients administered sodium nitroprusside can produce severe clinical symptoms, and concentrations above 4.4 mg/L are lethal.

Concentrations as low as 1 mg/L have been associated with cyanide poisonings (Niyogi, 1973), but such concentrations are often due to blood measurements taken after toxicity is observed or post mortem and

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are not reliable indications of the blood cyanide concentrations actually causing the toxicity.

Based on the totality of acute-toxicity data in humans, Scofield et al. (1988) concluded that a blood cyanide concentration of 0.5 mg/L is a reasonable threshold concentration for changes in blood chemistry and that clinical symptoms of cyanide intoxication are likely above a concentration of approximately 2 mg/L.

## CONCLUSIONS AND RECOMMENDATIONS

A blood cyanide concentration of 0.5 mg/L is considered nontoxic. By using a pharmacokinetic model and assuming that the blood cyanide concentration of 0.5 mg/L is nontoxic, the Army proposed field drinking-water standards for cyanide of 2 mg/L and 6 mg/L, assuming a water consumption of 15 L/day and 5 L/day, respectively. The subcommittee is in agreement with the Army's proposed standards. Therefore, the subcommittee's recommended field drinking-water guidelines for cyanide are the same as the Army's proposed standards.

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# Appendix A

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# *Criteria for Developing Field Drinking-Water Standards<sup>1</sup>*

## INTRODUCTION

**T**he U.S. Army in collaboration with the Lawrence Livermore National Laboratory developed drinking-water standards for several chemical warfare (CW) agent—organophosphorus nerve agents, cyanide, T-2 toxin, lewisite, sulfur mustard, and Agent BZ. In this chapter, the criteria used to develop the standards are presented (Daniels and Layton, 1988). The subcommittee considered these criteria in responding to its charge to review the Army's proposed field drinking-water standards. Based on its review of the proposed standards and the criteria used to develop the standards, the subcommittee concluded that the criteria used by the Army and Lawrence Livermore National Laboratory were adequate. However, some modifications were suggested. These suggestions are discussed in this appendix.

## CRITERIA FOR DEVELOPING FIELD DRINKING-WATER STANDARDS

Drinking-water standards for CW agents are developed to prevent

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<sup>1</sup>This appendix primarily comprises modified excerpts from Daniels and Layton (1988).

with physical abilities of gastrointestinal, cutaneous, and related to properly functioning and decision making; and emotions, discipline, motivation (Layton, 1988). Adverse effects and the poor quality of water with dissolved constituents and guidelines, involuntary decision of poor-quality water is the basic purpose of field drinking water in the performance of military personnel. To develop field drinking water in a consistent fashion, the Army is studying the characteristics of the water and exposure periods, data factors (Daniels and Layton,

#### Population at Risk

employed in the field. In general, males who are between 18 and 60 kg and are in good health. Personnel in the field were also considered between 18 and 55 years of age and in good health. The Army's recommendation is to protect all military personnel, not against performance-decay, but against health effects. These standards are not applicable to population water-quality standards for fixed installations (Daniels

#### Exposure Periods

of drinking water required by

military personnel to remain combat effective can range from about 5 to 15 L/d, depending on climate, season, and intensity of work (Henry, 1985). The duration over which consumption of field water will take place is divided into three scenarios: (1) short-term consumption lasting up to 7 consecutive days, (2) long-term consumption exceeding 7 days and lasting up to 1 year, and (3) emergency situations when soldiers are cut off from supply lines and treated water is not available. In these situations, troops are trained to select the cleanest water available and treat it with field expedient methods (U.S. Army, 1990, pp. 4-5). No standards apply for emergencies. Short-term standards for field drinking water are needed because drinking water that meets long-term standards might not be available in some battlefield situations. However, in the opinion of U.S. military and civilian experts, access to drinking water meeting the long-term standards is unlikely to be denied for more than 7 consecutive days. Long-term standards for field drinking water are applicable to forces deployed in military situations lasting up to 1 year; in those situations, military personnel would obtain the greatest proportion of their drinking water from military water-purification equipment, such as the reverse osmosis water purification unit. The DOD concluded that a 1-year duration for long-term field drinking-water standards was sufficient. The rationale for this conclusion is that within a year most of the drinking water consumed by field personnel should be provided by properly functioning fixed installations (Daniels and Layton, 1988). The subcommittee's charge was to consider "field" or "theater of operation" situations for time periods less than or equal to 7 days (i.e., short-term consumption).

#### Objectives of Field Drinking-Water Standards

The specific objectives of short- and long-term field drinking-water standards are defined by the Army (U.S. Army, 1986, 1990). These objectives are the cornerstone upon which the recommendations for field drinking-water standards are based (Daniels and Layton, 1988). Specifically, short-term standards are designed to protect against any health effect that can adversely affect the capability of an individual to conduct a military mission. However, as stated by the Army (U.S. Army, 1986), a field commander forced to institute short-term standards must acknowl-

edge the potential for reduced combat efficiency each day that short-term standards remain in effect; the risk of morbidity from prolonged exposure to field drinking water meeting short-term standards is greater than that to field water meeting long-term standards. Alternatively, long-term standards are designed to protect against any adverse health effects that appear during a 1-year exposure period. In combat situations, long-term adverse health effects (e.g., carcinogenesis, developmental and reproductive effects, and latent or chronic effects) are typically not as imminent or as consequential as performance decrements induced by immediate (i.e., acute) health effects. Nevertheless, potential chronic effects are identified in discussions accompanying the subcommittee's recommendations for guidelines if such information is available in the literature (Daniels and Layton, 1988).

### **Data Requirements**

When possible, toxicological data on humans following oral exposure are evaluated to ascertain dose-response relationships. If such human data are sparse, inadequate, or nonexistent, dose-response relationships for humans are extrapolated from oral dose-response data for animals. However, other routes of exposure in humans and animals were also considered by the subcommittee. The health effects resulting from synergistic interactions between chemicals of military concern are usually not considered because of the paucity of relevant data.

### **Toxic Effects**

Neither the existence or performance of water-quality monitoring devices nor the efficiency of water-purification equipment are a consideration in the development of the field drinking-water standards. The paramount concern is to develop and recommend standards that would prevent performance degradation from field drinking water consumed by military personnel deployed in field situations. Consequently, recommended standards do not protect against chronic health effects, such as carcinogenesis or developmental and reproductive effects (Daniels and

Layton, 1988). Based on the available toxicological data, the Army identified no-observed-adverse-effect levels (NOAELs) or lowest-observed-adverse-effect levels (LOAELs) for noncarcinogenic effects from studies in humans or animals. The highest NOAEL and LOAEL are identified for the most sensitive end point (target organ) and in the most sensitive species. When the literature did not contain NOAEL or LOAEL data, the Army used the available information, including data on the no-observed-effect level (NOEL) and the lowest-observed-effect level (LOEL).

### Uncertainty Factors

The Army used an uncertainty factor of 10 for interspecies (animal-to-human) extrapolation. However, the Army did not use an uncertainty factor for intraspecies (human-to-human) extrapolation because it assumed that all military personnel are healthy and do not have preexisting health conditions. The Army did not address the use of modifying factors to account for inadequate data or lack of data on certain toxic end points. When the data were not sufficient to identify a NOAEL, the Army used a NOEL or LOAEL and applied an uncertainty factor of 10.

### MODIFICATIONS TO FIELD DRINKING-WATER STANDARDS

The subcommittee reviewed the criteria used by the Army in deriving field drinking-water standards for CW agents. In general, these criteria are consistent with criteria used by EPA to develop drinking-water guidelines. Because the majority of the subcommittee agreed with the Army's criteria, it did not develop its own set of criteria as originally charged. However, certain modifications to the standards were suggested by the subcommittee. These modifications are discussed below and focus on the identification of concentrations at which critical toxicological effects occur.

The subcommittee did not agree with the Army's proposed field drinking-water standards for several of the organophosphorus nerve

agents—i.e., Agents GA, GB, GD, and VX. The drinking-water standards were based on 50% acetylcholinesterase (AChE) inhibition, which had been considered to be the NOEL. The subcommittee recommended 25% AChE inhibition as the NOEL for these substances.

The subcommittee did not agree with the methods used by the Army to derive field drinking-water standards for sulfur mustard. The Army based its proposed standards for sulfur mustard on an acute LOEL of 300  $\mu\text{g/kg}$  of body weight per day (Dacre and Burrows, 1988). This LOEL was identified as the concentration at which weight loss occurred in rats exposed to sulfur mustard for 90 days (Sasser et al., 1989). It was unclear to the subcommittee whether the weight loss was due to a toxic response or to reduced ingestion of food by experimental animals. The subcommittee did support consideration of 100  $\mu\text{g/kg/day}$  as the NOEL, as used in the drinking-water analysis by Dacre and Burrows (1988).

Furthermore, the procedure used by Dacre and Burrows to estimate the NOEL from data in the draft report by Sasser et al. (1989)—i.e., LOEL rating-effect value ( $RV_e$ )—is an unsubstantiated procedure and not endorsed by EPA. The  $RV_e$  is only used to calculate composite scores for determining reportable-quantity (RQ) estimates (EPA 1984). NOEL and LOEL values are to be already based on animal or human data from the literature.

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# Appendix B

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## *Capability for Detection of Chemical Warfare Agents in Field Drinking Water*

The standard method for monitoring chemical warfare (CW) agents in field drinking water is the M272 Chemical Agents Water Testing Kit developed by the Department of the Army (U.S. Army, 1983). Combat drinking-water standards established in 1975 (U.S. Army, 1975) were in effect at the time the M272 kit was first distributed for use in the field (May 1984). Concentrations of CW agents reliably detected by the kit are as follows: 20  $\mu\text{g/L}$  (0.02 mg/L) for organophosphate nerve agents; 2,000  $\mu\text{g/L}$  (2 mg/L) for vesicants (sulfur mustard and lewisite; lewisite measured as  $\text{As}^{+3}$ ); and 20,000  $\mu\text{g/L}$  (20 mg/L) for hydrogen cyanide (measured as  $\text{CN}^-$ ). The M272 kit does not test for Agent BZ or T-2 toxin.

These detection limits are adequate to measure concentrations at the current short-term field drinking-water standards for organophosphate nerve agents (20  $\mu\text{g/L}$ ), lewisite (2,000  $\mu\text{g/L}$  or 2.0 mg/L), and cyanide (20 mg/L) (U.S. Army, 1986). However, the kit's sensitivity is not adequate to measure concentrations at the current short-term standards for sulfur mustard (200  $\mu\text{g/L}$ ; difference of an order of magnitude (U.S. Army, 1986)) or any concentrations of Agent BZ or T-2 toxin.

Of the subcommittee's recommended field drinking-water guidelines (Table B-1), only those for the organophosphorus agent GA (70  $\mu\text{g/L}$  for 5 L/day water consumption and 22.5  $\mu\text{g/L}$  for 15 L/day water consumption) can be detected by the current protocol using the M272 kit. There

is a clear need for development of protocols and instrumentation to reliably detect the agents under review at the proposed field drinking-water concentrations.

**TABLE B-1** Summary of the Subcommittee's Recommended Field Drinking-Water Guidelines for Selected CW Agents in Field Drinking Water<sup>a</sup>

CW Agent	Recommended Guidelines	
	5 L/day	15 L/day
BZ ( $\mu\text{g/L}$ )	7.0	2.3
Organophosphorus nerve agents		
Agent GA ( $\mu\text{g/L}$ )	70.0	22.5
Agent GB ( $\mu\text{g/L}$ )	13.8	4.6
Agent GD ( $\mu\text{g/L}$ )	6.0	2.0
Agent VX ( $\mu\text{g/L}$ )	7.5	2.5
Sulfur mustard ( $\mu\text{g/L}$ )	140.0	47.0
T-2 toxin ( $\mu\text{g/L}$ )	26.0	8.7
Lewisite ( $\mu\text{g/L}$ ) (arsenic fraction) <sup>b</sup>	80.0	27.0
Cyanide (mg/L)	6.0	2.0

<sup>a</sup>Assumes a water consumption of up to 7 days.

<sup>b</sup>Based on detection of the arsenic fraction of lewisite in water; the corresponding concentration of lewisite is about 2.75 times greater.

## REFERENCES

- U.S. Army. 1975. Sanitary Control and Surveillance of Supplies at Fixed and Field Installations. TB MED 229. Department of the Army Headquarters, Washington, D.C.
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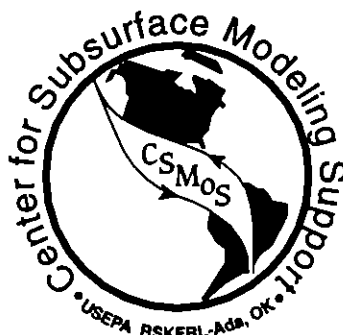
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# **VLEACH**

## **A One-Dimensional Finite Difference Vadose Zone Leaching Model**

**Version 2.2**



**Developed for:**

**The United States Environmental Protection Agency  
Office of Research and Development  
Robert S. Kerr Environmental Research Laboratory  
Center for Subsurface Modeling Support  
P.O. Box 1198  
Ada, Oklahoma 74820**

**By:**

**Varadhan Ravi and Jeffrey A. Johnson  
Dynamac Corporation**

**Based on the original VLEACH (Version 1.0)  
developed by CH<sub>2</sub>M Hill, Redding, California  
for USEPA Region IX**

## **Version 2.2a**

### **Differences Between version 2.2 and version 2.2a**

VLEACH version 2.2a is identical to version 2.2 except for a small correction on how the model calculates the mass (g/yr) in the "Total Groundwater Impact" section printed at the end of the main output file (\*.OUT). The mass rate (g/yr) is now the sum of all the columns (i.e., polygons) and not just the mass from the last column calculated.

## Version 2.2

### Differences between version 2.1 and version 2.2

VLEACH version 2.2 has two differences from the earlier release of the model. First, when using multiple columns in a simulation, the cumulative mass portion of the "Total Groundwater Impact" printed at the end of the \*.OUT file was incorrect. The cumulative mass now reflects the sum of the mass simulated from all columns instead of printing only the mass from the last column calculated.

Secondly, there has been significant discussions concerning the appropriate use of Millington's Equation (1959) when simulating gas diffusion within the vadose zone. Version 2.2 has been modified to reflect a more appropriate exponent in the equation. The exponent was changed from 10/3 to 7/3. For a more detailed discussion please read below:

The Millington Equation is a theoretical based model for gaseous diffusion in porous media, which was first developed by Millington (1959) and is given by:

$$\frac{D_e}{D_{air}} = n^2 \frac{(\psi_a)^{4/3}}{m^2} \quad (1)$$

with

$$\psi_a = \frac{n\psi}{m} \quad (2)$$

where  $D_e$  is gaseous diffusion coefficient in porous media,  $D_{air}$  is gaseous diffusion coefficient in free air,  $n$  is number of pores drained,  $\psi_a$  is air-filled porosity, and  $m$  is equal-volume pore size groups that make up porosity when  $n$  of them are drained.

Substituting Eq. (2) into (1) yields

$$\frac{D_e}{D_{air}} = \frac{(\psi_a)^{10/3}}{\psi^2} \quad (3)$$

Equation (3) is referred to as the Millington Equation and has been widely used in the fields of soil physics and hydrology to calculate the gaseous or vapor diffusion in porous media. This model has been shown to be in agreement with data over a wide range of soil water content (Sallam et al., 1984).

The development of Millington Equation was based on the theory of Fick's First Law. This law states that the diffusion flux of mass is a function of the diffusion coefficient in free air and the chemical concentration gradient and is given by:

$$J = D_{air} \frac{dC}{dZ} \quad (4)$$

where  $J$  is the diffusive mass flux,  $C$  is the chemical concentration in gas phase,  $Z$  is the distance, and  $D_{air}$  is the diffusion coefficient of the contaminant in free air.

When applying Fick's First Law to gaseous diffusion in a partially saturated porous medium such as soil, two factors must be considered: (1) the total spaces available for gaseous diffusion in a porous medium is less than that in free



air, due to the presence of the solid and liquid phases in the porous medium, and (2) the tortuosity of a porous medium, which is defined as the average ratio of actual roundabout path to the apparent, or straight, flow path. Therefore, Fick's First Law for gaseous diffusion in a partially saturated porous medium becomes:

$$J = D_e \frac{dC}{dz} \quad (5)$$

The gaseous diffusion coefficient,  $D_e$ , in this case is virtually an effective gaseous diffusion coefficient and is given by:

$$D_e = \psi_a D_p \quad (6)$$

where  $D_p$  is the gaseous diffusion coefficient in air-filled pore spaces only. Substituting Equation (6) into Equation (3) yields:

$$\frac{D_p}{D_{air}} = \frac{(\psi_a)^{2/3}}{\psi^2} \quad (7)$$

Equation (7) is an expression of Millington Equation for calculating gaseous diffusion coefficient in air-filled pore spaces. This equation has been used by Falta et al (1992) and Shan and Stephens (1995). Since the VLEACH model considered the gaseous diffusion only in the air-filled pore spaces, a correct use of the Millington Equation should be Equation (7). Comparison of Equations (3) and (7) reveals that Equation (3) underestimates the gaseous diffusion coefficient. This will lead to a longer arrival time of contaminants to the groundwater table. A similar observation was also reported by Javaheran (1994).

It should be noted that the Millington Equation is not the only equation used for calculating the gaseous diffusion coefficient in porous media. There are varieties of equations used in the literature to represent the diffusion of gases in porous media (Currie, 1960; Troeh et al., 1982; Collin and Rasmuson, 1988; Freijer, 1994). Interested readers are encouraged to consult these publications for a comprehensive understanding of gaseous diffusion coefficient in porous media.

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# **VLEACH:**

## **A One-Dimensional Finite Difference Vadose Zone Leaching Model**

### **Version 2.1**

Addendum to the VLEACH 2.0 User's Guide

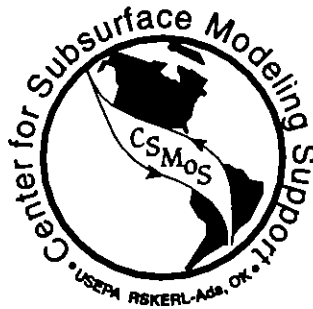
VLEACH version 2.1 incorporates the following changes from version 2.0:

- 1) the addition of the English.eer file, which is an error message file, and
- 2) the correction of a printing error associated with the groundwater impact output.

# **VLEACH**

## **A One-Dimensional Finite Difference Vadose Zone Leaching Model**

**Version 2.0**



**Developed for:**

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## **DISCLAIMER**

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency. However, it has not yet been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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Appendix A-Simulation Parameter Information

Appendix B-Polygon Parameter Information

Appendix C-Reference Information

Appendix D-Output Results from the Sample Problem

Appendix E-Model Data Sheet

## **ACKNOWLEDGEMENT**

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## 1. INTRODUCTION

VLEACH, A One-Dimensional Finite Difference Vadose Zone Leaching Model, is a computer code for estimating the impact due to the mobilization and migration of a sorbed organic contaminant located in the vadose zone on the underlying groundwater resource. The model was initially developed by CH<sub>2</sub>M Hill for the U.S. Environmental Protection Agency, Region IX in 1990. In particular, the model was designed specifically on the Phoenix-Goodyear Airport Superfund site where it was used successfully to evaluate groundwater impacts and volatilization of volatile organic contaminants (Rosenbloom et al., 1993). Since that time the code has been utilized at numerous sites to assess the potential groundwater impacts from existing soil contaminants and in soil vapor projects. Due to the increasing use of VLEACH, work was conducted to develop a more user-friendly version of the software along with a more comprehensive user's guide. In particular, version 2.0 incorporates the following changes from version 1.1:

- 1) the addition of an user interface menu;
- 2) the user can specify any input file name rather than always having to define the file as "BATCH.INP";
- 3) the development of two plot files: (i) groundwater impact as a function of time and (ii) soil concentration versus depth at a user-specified time;
- 4) units for  $C_{sol}$  were added to the output file printout; and
- 5) a common statement, "COMMON/BDRY/CINF, CATM, CGW", which defines the boundary condition parameter was added to the IEQUIL subroutine.

Although VLEACH employs a number of major assumptions, it can be useful in making preliminary assessments of the potential impacts of contaminants within the vadose zone. Hence, it is the principle objective of the User's Guide to provide essential information on such important aspects as model conceptualization, model theory, assumptions and limitations, determination of input parameters, analysis of results and sensitivity analysis (parameter studies). It is anticipated that the information presented in this manual will aid the model user in making the best possible application of VLEACH.





## **2. MODEL CONCEPTUALIZATION, ASSUMPTIONS, AND LIMITATIONS**

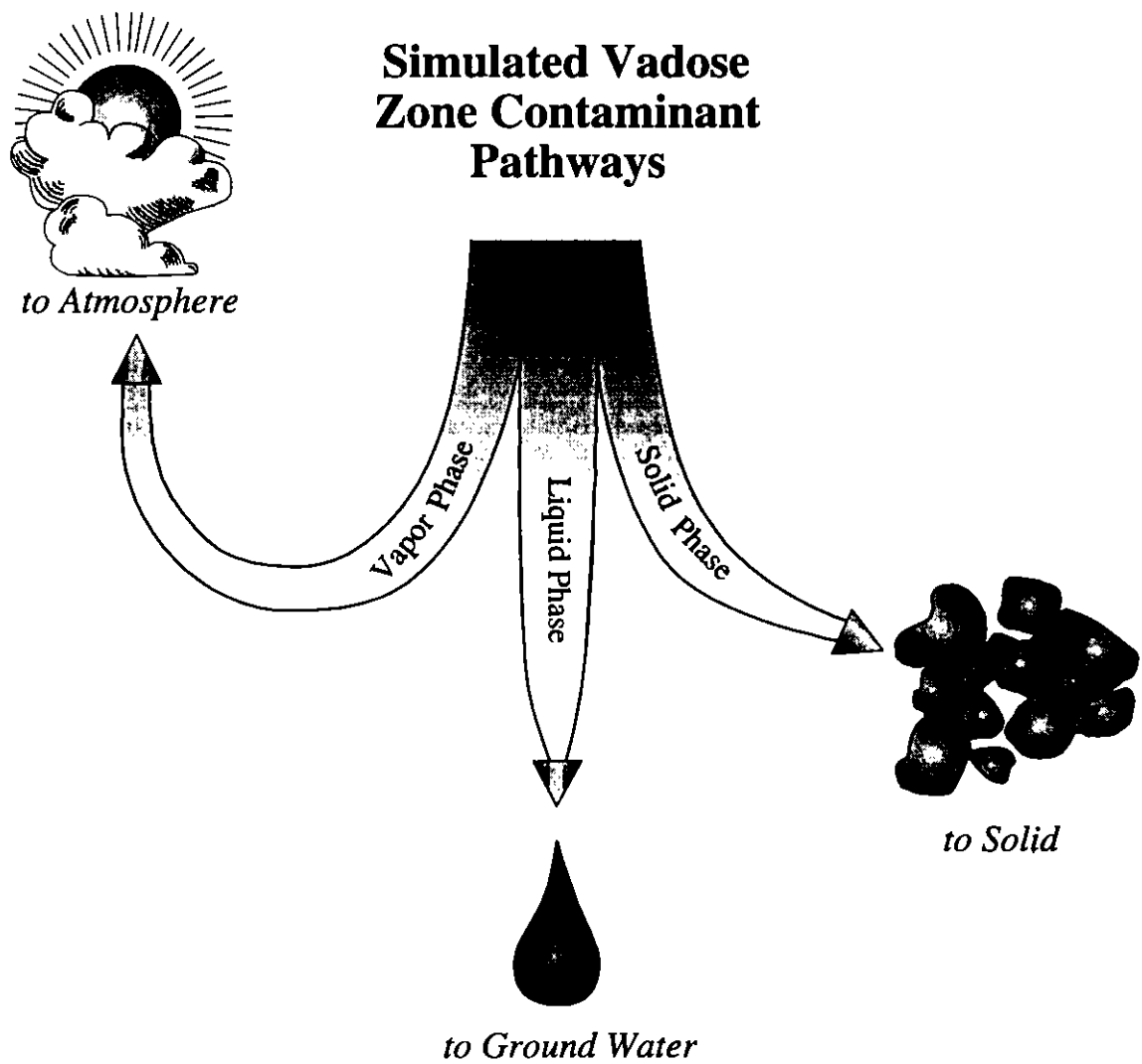
VLEACH describes the movement of an organic contaminant within and between three different phases: (1) as a solute dissolved in water, (2) as a gas in the vapor phase, and (3) as an adsorbed compound in the solid phase (see Figure 1). Equilibration between the phases occurs according to distribution coefficients defined by the user. In particular, VLEACH simulates vertical transport by advection in the liquid phase and by gaseous diffusion in the vapor phase.

These processes are conceptualized as occurring in a number of distinct, user-defined polygons that are vertically divided into a series of user-defined cells. The polygons may differ in soil properties, recharge rate, and depth to water (see Figure 2). However, within each polygon homogeneous conditions are assumed except for contaminant concentration, which can vary between layered cells (see Figure 3). During each time step the migration of the contaminant within and between cells is calculated. Hence, VLEACH can account for heterogeneities laterally but is limited when simulating vertical heterogeneity.

Initially, VLEACH calculates the equilibrium distribution of contaminant mass between the liquid, gas, and sorbed phases. Transport processes are then simulated. Liquid advective transport is calculated based on values defined by the user for infiltration and soil water content. The contaminant in the vapor phase migrates into or out of adjacent cells based on the calculated concentration gradients that exist between adjacent cells. After the mass is exchanged between the cells, the total mass in each cell is recalculated and re-equilibrated between the different phases. These steps are conducted for each time step, and each polygon is simulated independently. At the end of the model simulation, the results from each polygon are compiled to determine an overall area-weighted groundwater impact for the entire modeled area.

For computational purposes each polygon is divided vertically into a series of cells. When developing a model simulation, it is important to fully understand the implications of the VLEACH conceptualization. The following assumptions are made in the development of VLEACH.

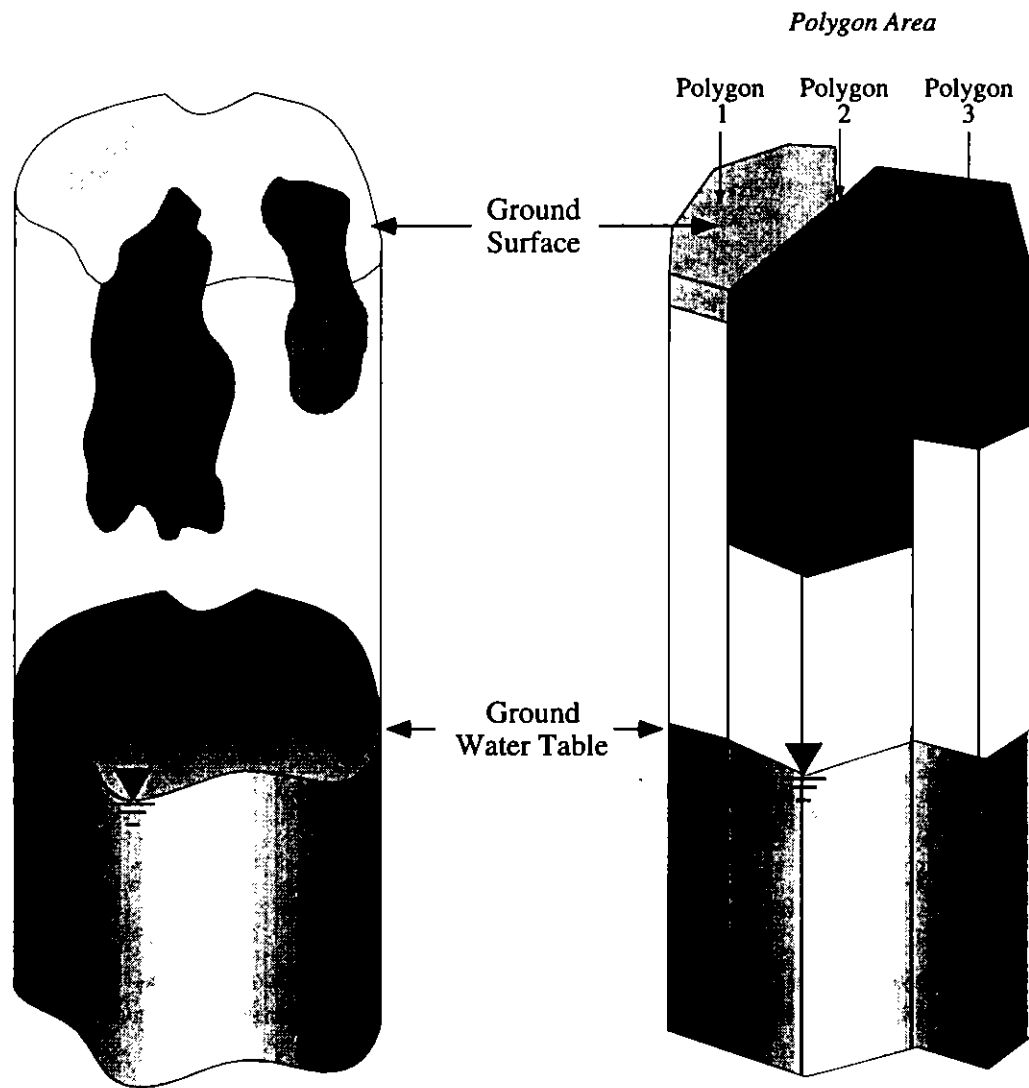
1. Linear isotherms describe the partitioning of the pollutant between the liquid, vapor and soil phases. Local or instantaneous equilibrium between these phases is assumed within each cell.
2. The vadose zone is in a steady state condition with respect to water movement. More specifically, the moisture content profile within the vadose zone is constant. This assumption will rarely occur in the field. Although moisture gradients cannot be simulated, the user can estimate the impact of various moisture contents by comparing results from several simulations that cover the common or possible ranges in soil moisture conditions.



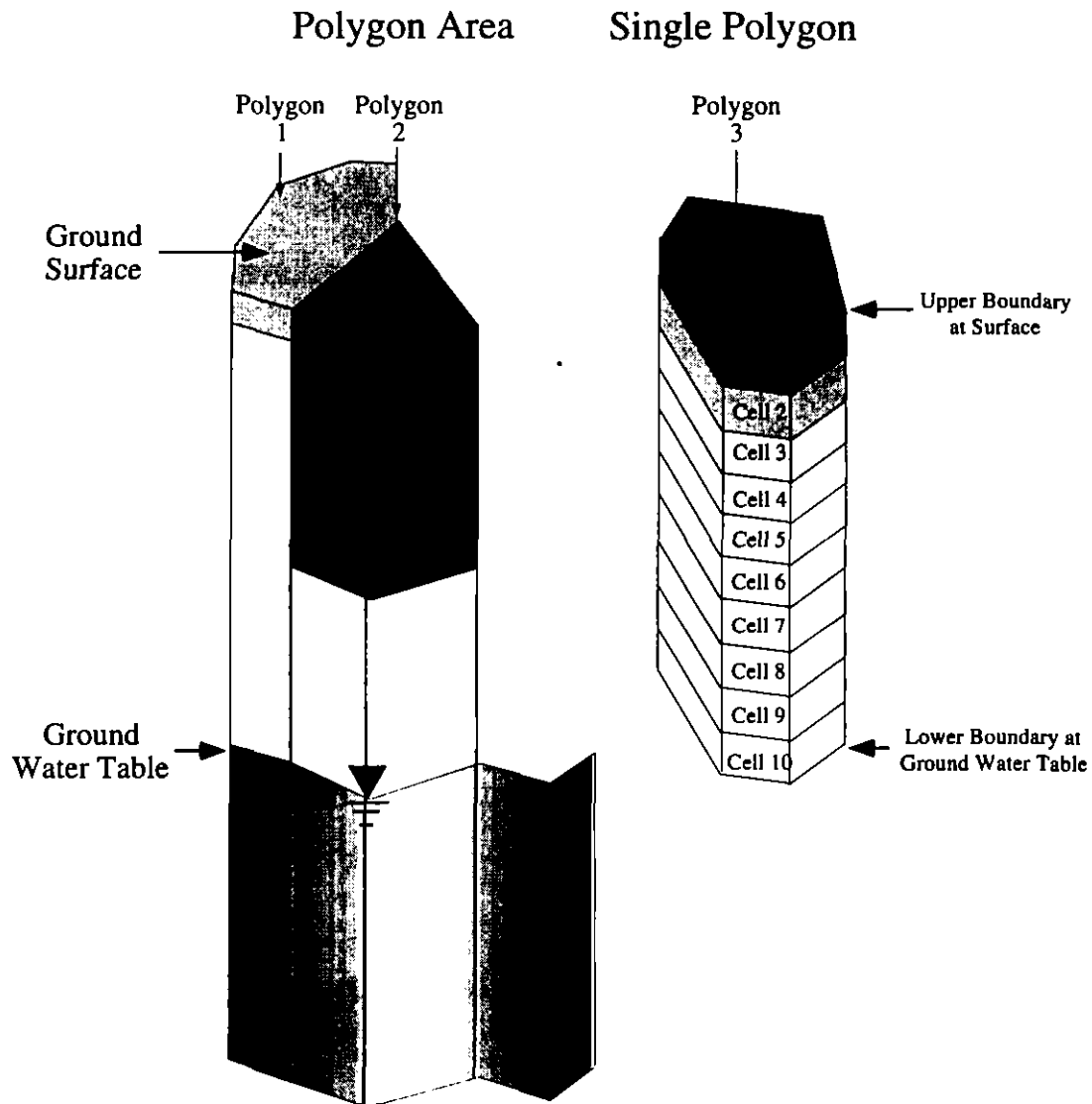
**Figure 1.** Schematic diagram illustrating the contaminant pathways simulated by VLEACH

A. Site Conditions

B. Model Conceptualization



**Figure 2.** Schematic diagram illustrating model conceptualization as polygons due to variations in site conditions.



**Figure 3.** Schematic diagram illustrating the delineation of cells within a single polygon. The variation in shading within the upper three cells represent differences in contaminant concentrations.

3. Liquid phase dispersion is neglected. Hence, the migration of the contaminant will be simulated as a plug. This assumption causes higher dissolved concentrations and lower travel time predictions than would occur in reality.

4. The contaminant is not subjected to in situ production or degradation. Since organic contaminants, especially hydrocarbons, generally undergo some degree of degradation in the vadose zone, this assumption results in conservative concentration values.
5. Homogeneous soil conditions are assumed to occur within a particular polygon. This assumption will rarely occur in the field. Although spatial gradients cannot be simulated, the user can estimate the impact of non-uniform soils by comparing results from several simulations covering the range of soil properties present at the site. However, initial contaminant concentrations in the soil phase can vary between cells.
6. Volatilization from the soil boundaries is either completely unimpeded or completely restricted. This assumption may be significant depending upon the depth of investigation and the soil type. In particular, after a depth of 1 meter volatilization to the atmosphere will decrease significantly.
7. The model does not account for non-aqueous phase liquids or any flow conditions derived from variable density.



### 3. MATHEMATICAL DISCUSSION

VLEACH treats spatial and temporal variation of contaminant concentration in solid, liquid, and gas phases. These variables are denoted as  $C_s(z,t)$ ,  $C_l(z,t)$  and  $C_g(z,t)$ , respectively, where  $z$  and  $t$  stand for the space and time variables. The total contaminant mass initially (prior to infiltration of water) present in the soil is assumed to be dissolved into the liquid phase. This yields the following relation:

$$C_l(Z,0) = M(Z,0) \frac{\rho_b}{\theta} \quad (1)$$

where  $C_l(z,0)$  is the initial liquid phase contaminant concentration (g/ml),  $M(z,0)$  is the initial mass of contaminant per unit mass of soil at location  $z$  (g/g of soil),  $\theta$  is the volumetric water content, and  $\rho_b$  is the bulk density of soil (g/ml).

The concentration in the liquid phase is obtained by solving the following equation which accounts for advection given  $C_l(z,0)$ :

$$\frac{\partial C_l}{\partial t} = -\frac{q}{\theta} \frac{\partial C_l}{\partial z} \quad (2)$$

In Eq. (2),  $q$  is the Darcy velocity of infiltrating water. The gas phase concentration of contaminant is determined by the following diffusion equation:

$$\frac{\partial C_g}{\partial t} = D \frac{\partial^2 C_g}{\partial z^2} \quad (3)$$

where  $D$  is the effective diffusion coefficient of contaminant in gas phase. The above equation is solved with appropriate initial and boundary conditions. After the evaluation of  $C_l(z,t)$  and  $C_g(z,t)$ , the equilibrium concentration of the contaminant in the three phases is determined as follows.

First the total mass in the soil  $M_T$  is calculated:

$$M_T(z,t) = [\theta C_l + (\phi - \theta) C_g + \rho_b C_s] \quad (4)$$

where  $\phi$  is the soil porosity. Then the individual phase concentrations are evaluated using the following relations.

$$C_s(z, t) = \frac{K_H M_T(z, t)}{[\theta + (\phi - \theta)K_H + K_d \rho_b]} \quad (5)$$

$$C_l(z, t) = \frac{M_T(z, t)}{[\theta + (\phi - \theta)K_H + K_d \rho_b]} \quad (6)$$

$$C_g = \frac{K_d M_T(z, t)}{[\theta + (\phi - \theta)K_H + K_d \rho_b]} \quad (7)$$

The partial differential equations (2) and (3) are solved using an implicit, finite-difference numerical scheme. The distribution coefficient  $K_d$  (ml/g) and gas phase diffusion coefficient  $D$  (m<sup>2</sup>/day) are calculated using the following empirical relations:

$$K_d = K_{oc} f_{oc} \quad (8)$$

$$D = D_{air} \frac{(\phi - \theta)^{10/3}}{\phi^2} \quad (9)$$

where  $K_{oc}$  is the organic carbon partition coefficient of the contaminant and  $f_{oc}$  is the fraction organic carbon content of the soil, and  $D_{air}$  is the free-air diffusion coefficient of the contaminant.



## **4.0 HARDWARE AND SOFTWARE REQUIREMENTS**

The minimum hardware and software requirements for VLEACH version 2.0 are:

- IBM-PC or compatible computer with INTEL 8086, 80286, 80386, or 80486 CPU based system
- 256K RAM
- Color Graphic Adapter (CGA) board
- One floppy disk drive
- (MS/PC) DOS 2.0 or higher

Additional recommended hardware and software include:

- A math coprocessor
- A hard disk
- A FORTRAN Compiler for modifications of the source code
- A commercial graphics software such as Grapher by Golden Software, Inc.



## 5.0 GETTING STARTED

VLEACH version 2.0 is distributed by the EPA's Center for Subsurface Modeling Support (CSMoS) on a single IBM-formatted 3 1/2-inch diskette. VLEACH version 2.0 includes the following 16 files.

THOMAS.FOR	VLEACH.FOR
VLEACH.EXE	SAMPLE.INP
TEST.INP	SAMPLE.OUT
SAMPLE.PRF	SAMPLE.PRM
SHOW.EXE	FORMENU2.TXT
FORMENU1.TXT	CHGNAME.TXT
VLMENU.BAT	SOILIMP.DAT
GWIMP.DAT	WHAT.EXE

Prior to installing or implementing the program make a back-up copy of VLEACH. Once completed, copy the VLEACH files to the hard disk in a selected directory. Because the program requires ample storage for the output files, the program should be run from the C drive. In addition, a text editor will have to be defined in the AUTOEXEC.BAT file. The text editor could be DOS edlin, DOS edit, Norton Classic editor, WordPerfect, or any other commercial editor. Define the text editor in AUTOEXEC.BAT (including its path), for example,

```
SET EDITOR=C:\WP51\WP
```

Finally, the ANSI.SYS driver (see your MS-DOS manual) must be installed in the CONFIG.SYS file. This is done by adding a statement such as

```
DEVICE=C:\DOS\ANSI.SYS
```

It is important that the correct path for ANSI.SYS be given.

## 5.1 Program Execution

VLEACH version 2.0 is executed by typing <VLMENU> at the appropriate directory prompt. VLEACH must be run only from the menu. Do not try to execute the code by typing "Vleach" as code will not work properly.

C:\VLMENU

This will initiate the model execution, and a menu of options will be displayed on the screen.

---

### VLEACH PREPROCESSOR Welcome to VLEACH Version 2.0

Current Working File: NONE.INP

- 1 - List of input files
- 2 - List current directory
- 3 - Select an input file
- 4 - View the input file
- 5 - Edit/Create input file
- 6 - Run the VLEACH program
- 7 - View the output (.OUT) file
- 8 - View the profile (.PRF) file
- 9 - Print input data (.PRM) file
- 10 - Print output (.OUT) file
- 11 - Print profile (.PRF) file
- D - Go to DOS (enter EXIT to Return)
- Q - Quit the menu

Please enter your selection:

---

Select an option by typing the appropriate number or letter. Hit ENTER, the code will automatically continue.

## 6.0 INPUT PARAMETERS

The following describes the input parameters for VLEACH. It is important that this information be fully understood for proper application of the code. The input parameters for VLEACH consist of two groups, simulation data and polygon-specific data. The simulation data are defined once per model run while the polygon-specific data are defined for per each polygon. In the parameter descriptions below, the FORTRAN format, which is used in data entry, is presented in order of designation per card for the input data.

### 6.1 Simulation Data

- a. **Title.** A title of up to 80 characters can be defined that describes the simulation. The title will be printed with each output file. [Card 1: TITLE (A80)]
- b. **Number of Polygons.** The number of polygons conceptualized for the site. Each polygon will have a unique set of parameter data. [Card 2: NPOLY (I3)]
- c. **Timestep.** The model timestep given in years. [Card 3: DELT (G10.0)]
- d. **Simulation Time.** The total time length of the simulation given in years. [Card 3: STIME (G10.0)]
- e. **Output Time Interval.** The time interval at which the ground-water impact and mass balance results are printed to the .OUT file. The output time interval is in years. [Card 3: PTIME (G10.0)]
- f. **Profile Time Interval.** The time interval at which the vertical concentration profile results are printed to the .PRF file. The profile time interval is in years. [Card 3: PRTIME (G10.0)]
- g. **Organic Carbon Distribution Coefficient ( $K_{oc}$ ).** The organic carbon distribution coefficient describes the partitioning of the contaminant with organic carbon. The coefficient is in units of ml/g. Appendix A lists the values of  $K_{oc}$  for numerous contaminants. If data regarding the pollutant being modeled is not presented refer to the standard reference manuals that are documented in Appendix C or consult the manufacturer of the compound. [Card 4: KOC (G10.0)]
- h. **Henry's Constant ( $K_H$ ).** Henry's constant is an empirical constant that describes the liquid-gas partitioning of the contaminant. Henry's constant is a function of the solubility and partial vapor pressure of the contaminant at a given temperature. VLEACH utilizes the dimensionless form of Henry's constant given as

$$\frac{M/L^3_{AIR}}{M/L^3_{WATER}}$$

The dimensionless form of  $K_H$  can be determined from the more common form having the units of atmospheres-cubic meters per mole ( $\text{atm}\cdot\text{m}^3/\text{mol}$ ) using the following equation

$$K_H = K_H' / 0.0246 \quad \text{at } 27^\circ\text{C}$$

where  $K_H$  is dimensionless and  $K_H'$  is in units of  $\text{atm}\cdot\text{m}^3/\text{mol}$ . Data regarding Henry's Law Constant for over 60 common volatile and semi-volatile organic compounds are provided in Appendix A. [Card 4: KH (G10.0)]

- i. **Water Solubility.** Values defining the water solubility of the contaminant must have units of milligrams per liter (mg/L). Appendix A provides water water solubility information for over 60 compounds. [Card 4: CMAX (G10.0)]
- j. **Free Air Diffusion Coefficient.** The free air diffusion coefficient describes transfer of the contaminant due to Brownian motion in the air phase. The coefficient is in meter<sup>2</sup> per day ( $\text{m}^2/\text{day}$ ). For information regarding the free air diffusion coefficient refer to Bird et al. (1960)(pp. 503-514), or any similar reference text. [Card 4: DAIR (G10.0)]

## 6.2 Polygon Data (this set is repeated NPOLY times)

For each polygon input values for the following parameters are needed.

- k. **Title.** A title of up to 80 characters can be defined that describes the simulation. The title will be printed with each output file. [Card 1: TITLE (A80)]
- l. **Area.** This parameter defines the area of the polygon in square feet. [Card 2: AREA (G10.0)]
- m. **Vertical Cell Dimension.** This parameter defines the vertical height of the cells within the polygon. The cell dimension is in feet. [Card 2: DELZ (G10.0)]
- n. **Recharge Rate.** The groundwater recharge rate describes the velocity of water movement through the vadose zone. The rate is given in feet per year. In the vadose zone the hydraulic conductivity of the soil is an increasing function of the water content of the soil. Hence, the ground water recharge rate should be equal to or lower than the hydraulic conductivity of the soil at the modeled water content. It should be noted that this parameter is extremely difficult to estimate as in reality it will vary with respect to time. It is strongly suggested that a range of possible recharge values be utilized to evaluate the potential variability of the results due to uncertainty associated with this parameter. [Card 2: Q (G10.0)]

- o. **Dry Bulk Density.** This parameter describes the mass of dry soil relative to the bulk volume of soil. It is described in units of grams per cubic centimeters ( $\text{g}/\text{cm}^3$ ). Ranges for bulk density with respect to different soil types are given in Appendix B. [Card 2: RHOB (G10.0)]
- p. **Effective Porosity.** The effective porosity describes the volume of void space within the soil that is potentially fillable with water. The effective porosity equals total porosity minus irreducible water content, that percentage of total volume that water is retained due to capillary forces (see Appendix B). Effective porosity is a dimensionless parameter. [Card 2: POR (G10.0)]
- q. **Volumetric Water Content.** The water content of the soil in percent total volume. This parameter is assumed constant in time and space, however, this rarely occurs in nature. The volumetric water content can neither exceed the porosity of the soil nor be lower than the irreducible soil water content. [Card 2: THETA (G10.0)]
- r. **Soil Organic Carbon Content.** The fraction organic content of the soil is the relative amount of organic carbon present in the soil. This parameter defines the amount of potential adsorptive sites for the contaminant in the solid phase. The fraction organic content can be determined from laboratory analyses or is documented in some soil descriptions of the Soil Conservation Service. Generic values for organic content for soils of different texture are listed in Appendix B. [Card 2: FOC (G10.0)]
- s. **Concentration of Recharge Water.** This parameter defines the contaminant concentration in milligrams per liter ( $\text{mg}/\text{L}$ ). If the recharge water is derived from precipitation the contaminant concentration will typically be set at zero. [Card 3: CINF (G10.0)]
- t. **Upper Boundary Condition for Vapor.** This parameter defines the contaminant concentration in  $\text{mg}/\text{L}$  in the atmosphere above the soil surface. If the upper boundary of the polygon is considered impermeable to gas diffusion enter a negative value. [Card 3: CATM (G10.0)]
- u. **Lower Boundary Vapor Condition for Vapor.** This parameter defines the contaminant concentration in  $\text{mg}/\text{L}$  in the ground water at the base of the vadose zone. If the lower boundary of the polygon is considered impermeable to gas diffusion enter a negative value. [Card 3: CGW (G10.0)]
- v. **Cell Number.** The cell number defines the number of cells within the polygon. The number of cells is equal to the polygon height divided by the Cell Vertical Dimension. [Card 4: NCELL (I5)]
- w. **Plot Variable.** Variable to denote the plotting option. "Y" or "y" indicates that a plot file containing the soil contaminant profile will be created. [Card 4: PLT (A1)]

- x. **Plot Time.** Plot time defines the time in years for which the soil contaminant profile data will be created for the plot file. [Card 4: PLTIME (G10.0)]
- y. **Initial Contaminant Concentration.** This value defines the initial contaminant concentration in the soil within a single or set of cells. The concentration is given in units of micrograms per kilogram (ug/kg). The input is given by recording the number of the upper and the lower cells (J1 and J2, respectively) and the defined concentration (XCON) in those cells. The initial contaminant concentration must be defined for all cells within the polygon. [Card 5: J1,J2, XCON (2I5,G10.0) Card 5 is repeated as necessary until each cell has been described and the bottom cell (J2) equals the Cell Number (NCELL)].

The arrangement of the input data within the input file is shown in Figure 4. The spacings for the input are designated by the alphabetical letter identifying the input parameter listed above. For example the input parameter "Simulation Time," which is identified by the letter "d", is defined on line 3 from columns 11 through 20. Due to the number of variables defined in the parameter, "Initial Contaminant Concentration," this parameter is designated in Figure 4 as: J1 = \*, J2 = #, and XCON = \$.

---

```

aaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaa
bbb
ccccccccccddddddeeeeeeeeffffffff
ggggggggghhhhhhhhhiiiiiiijjjjjj
kkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkkk
llllllllmmmmmmmmmmnnnnnnnnnoooooooooopppppppppqqqqqqqqrrrrrrrrr
sssssssstttttttuuuuuuuuu
vvvvvwwxxxxxxxxx
*****#####$$$$$$$$$

```

---

**Figure 4.** Schematic diagram illustrating the arrangement of the VLEACH input file. The alphabetical letters refer to the model input parameters, which are discussed in Sections 6.1 and 6.2.



## 7.0 OUTPUT

### 7.1 Output Options

An option can be defined by the user to convert the output from VLEACH into files that can be plotted using GRAPHIER (Golden Software, 1987) or other compatible commercial graphics packages. Two graphs can be constructed: a groundwater impact curve and a soil-depth contaminant concentration profile. These can be selected by defining a "Y" or "y" for the input parameter, Plot Variable, (see Section 6.2.w). This creates two ASCII data files in X-Y format, GWIMP.DAT and SOILIMP.DAT. If plots are desired then input the time in years at which the soil concentration profile will be defined for the Plot Time Variable (see Section 6.2.x).

### 7.2 Output Results

VLEACH output provides information regarding the input parameters, the physical nature of the vapor, liquid, and solid contaminant mass balances in the soil, ground-water impacts from the contaminant, and the concentration profile of the contaminant within the soil profile. The output consists of three different files having the extensions .PRM, .OUT, and .PRF. The code allows the user to view the output as well as to print the output. These options can be selected from the main menu screen.

#### 7.2.1 \_\_\_\_\_.PRM File

The initial output file is the .PRM file, which is a summary of the model scenario. The information presented includes the title of the scenario and the input parameter values. The .PRM file should be closely reviewed to ensure that the appropriate values were utilized in the simulation. An example of the .PRM file input summary is given below.

---

```
Sample Problem - TCE contamination scenario
1 polygons
Timestep = 10.00 years. Simulation length = 500.00 years
Printout every 100.00 years. Vertical profile stored every 250.00 years.
Koc = 100.00 ml/g. .35314E-02cu.ft./g
Kh = .40000 (dimensionless).
Aqueous solubility = 1100.0 mg/l, 31.149 g/cu.ft
Free air diffusion coefficient = .70000 sq. m/day, 2750.3 sq.ft./yr

Polygon 1
Polygon I
Polygon area = 1000.0 sq. ft
50 cells, each cell 1.00 ft. thick.
Soil Properties:
Bulk density = 1.6000 g/ml 45307 g/cu.ft.
Porosity = .4000 Volumetric water content = .3000
Organic carbon content = .3000
Recharge Rate = 1.00000000 ft/yr
Conc. in recharge water = .00000 mg/l, .00000 g/cu.ft
Atmospheric concentration = .00000 mg/l, .00000 g/cu.ft
Water table has a fixed concentration of .00000 mg/l, .00000 g/cu.ft with respect to gas diffusion.
```

---

### 7.2.2 \_\_\_\_\_.OUT File

The .OUT file contains mass balance and groundwater impact data. In particular the calculated mass in the vadose zone as well as each phase is presented for each time defined interval within each polygon. The mass is calculated in grams/square foot (g/sq. ft.). An example of the output describing the mass balance data for the vadose zone as well as each phase is shown below.

---

#### Test Problem - TCE contamination scenario

##### Polygon 1

At time = 100.00, total mass in vadose zone	= .13162E-01 g/sq.ft.
Mass in gas phase	= .46184E-03 g/sq.ft.
Mass in liquid phase	= .34638E-02 g/sq.ft.
Mass sorbed	= .92368E-02 g/sq.ft.

---

For all time intervals after the initial interval, the change in total mass since the previous printed time level as well as the cumulative change in total mass since the initial conditions are presented. The components of the changes in mass are described as advection in from the atmosphere, advection in from water table, diffusion in from atmosphere, diffusion in from water table, total inflow at boundaries, and mass discrepancy. A positive value in the mass change indicates a net mass gain to the soil system, and a negative value indicates a mass loss from the system. An example of the output file description of the changes in mass balance data is given below.

---

Since last printout at time	= .00
Change in Total Mass	= -.10463 g/sq.ft.
Advection in from atmosphere	= .00000 g/sq.ft.
Advection in from water table	= -.97914E-01 g/sq.ft.
Diffusion in from atmosphere	= -.34935E-02 g/sq.ft.
Diffusion in from water table	= -.32245E-02 g/sq.ft.
Total inflow at boundaries	= -.10463 g/sq.ft.
Mass discrepancy	= 0.29802E-07 g/sq.ft.

Since beginning of run at time 0.0	
Change in Total Mass	= -.10463 g/sq.ft.
Advection in from atmosphere	= .00000 g/sq.ft.
Advection in from water table	= -.97914E-01 g/sq.ft.
Diffusion in from atmosphere	= -.34935E-02 g/sq.ft.
Diffusion in from water table	= -.32245E-02 g/sq.ft.
Total inflow at boundaries	= -.10463 g/sq.ft.
Mass discrepancy	= 0.29802E-07 g/sq.ft.

---

The final section of the .OUT file is the presentation of the groundwater impact data. This information is given for each polygon, i.e. "groundwater impact of polygon 1" as well as for the entire area, i.e. "total groundwater impact." The groundwater impact data for the polygon are calculated for each printout interval and are given as mass per area (g/sq.ft.) and total mass (g). The total groundwater impact is defined in terms of total mass and cumulative mass per printout interval. The example below illustrates the presentation of the groundwater impact data presentation.

---

GROUNDWATER IMPACT OF POLYGON 1

Time	Mass per area (g/sq.ft.)	Total Mass (g)
100.00	.10114	101.14
200.00	.12749E-01	12.749
300.00	.35681E-03	.35681
400.00	.62807E-05	.62807E-02
500.00	.95043E-07	95043E-04

\*\*\*\*\*  
\*\*\*\*\*

TOTAL GROUNDWATER IMPACT

Time	Mass (g)	Cumulative Mass (g)
100.00	101.14	101.14
200.00	12.749	113.89
300.00	.35681	114.24
400.00	.62807E-02	114.25
500.00	.95043E-04	114.25

---

The .PRF output describes the contaminant concentration profile within the defined vadose zone for the vapor, liquid, and solid phases. The profile data are presented as a series of tables for each cell within the polygon at the designated time interval. The output tabulation lists four columns: (1) cell number, (2) vapor concentration ( $C_{gas}$ ), (3) liquid concentration ( $C_{liq}$ ), and (4) solid concentration ( $C_{sol}$ ). An example of the concentration profile tabulation is shown below.

---

Polygon 1

Time: 500.00

Cell	Cgas (g/cu.ft)	Clq (g/cu.ft)	Csol (g/g)
1	.19048E-13	.47620E-13	.84083E-18
2	.41161E-13	.10290E-12	.18170E-17
3	.66829E-13	.16707E-12	.29500E-17
.	.	.	.
.	.	.	.
.	.	.	.
49	.41901E-10	.10475E-09	.18497E-14
50	.45453E-10	.11363E-09	.20064E-14

---

### **7.3 Graphical Output Displays**

Using commercial graphics packages two graphs can be plotted using the output from the model simulation. VLEACH automatically writes output data to two files named GWIMP.DAT and SOILIMP.DAT for plotting purposes. The file GWIMP.DAT contains the mass rate of contaminant loading to the groundwater versus time array. When plotted the mass loading is defined on the Y-axis while time is defined on the X-axis. The file SOILIMP.DAT contains the values for contaminant concentration sorbed to the soil versus depth array for the specified time period. When plotted the contaminant concentration is defined on the X-axis and depth is given on the Y-axis. Examples of the plots are shown in the Sample Problem, Section 9.0.

## 8.0 SENSITIVITY ANALYSIS

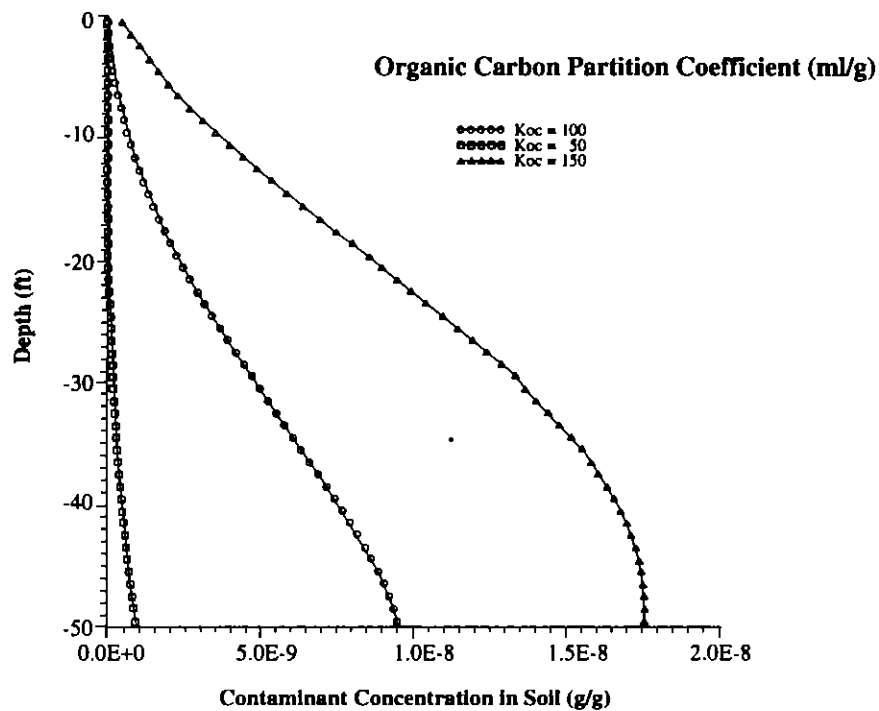
A sensitivity analysis was performed to evaluate the impact of various input parameters on soil contaminant level and loading to groundwater. The results of the study are depicted in Figures 8.1 through 8.18. It is seen that the organic carbon partition coefficient ( $K_{oc}$ ), infiltration velocity ( $q$ ), and fraction organic carbon ( $f_{oc}$ ) have the greatest impact on both soil contaminant concentration and groundwater loading. Bulk density ( $\rho_b$ ) and porosity ( $\phi$ ) have a significant effect only on the soil contaminant level. The other parameters are found to have no significant impact on either soil contaminant level or groundwater loading. A qualitative description of the sensitivity of each parameter to the calculated groundwater impact and soil concentration profile are compiled in the tables below.

**VLEACH PARAMETER SENSITIVITY TO SOIL CONCENTRATION PROFILE**

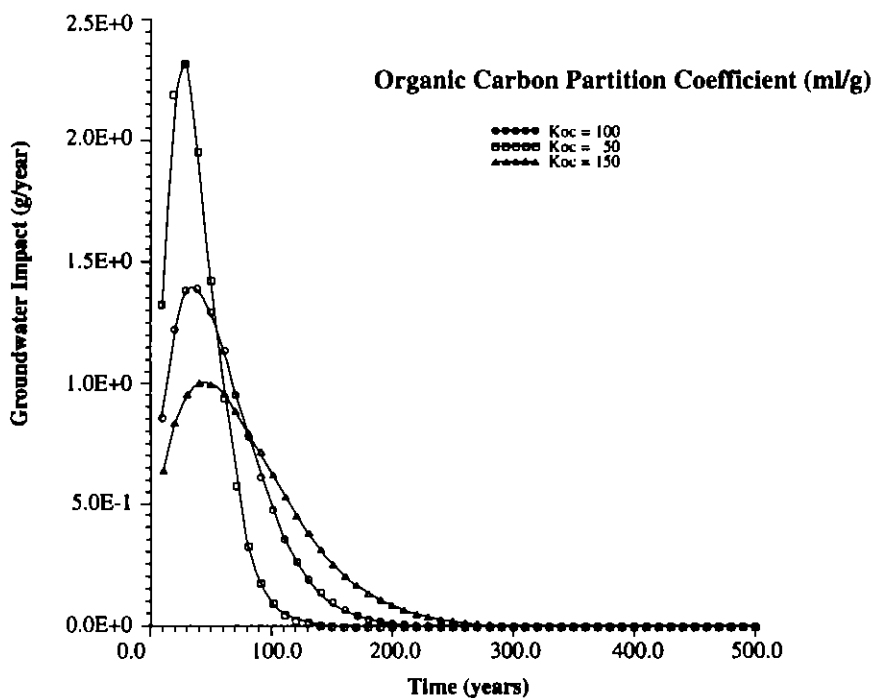
	$K_{oc}$	$K_H$	$C_{sol}$	$D_{air}$	$q$	$\rho_b$	$\phi$	$\theta$	$f_{oc}$
High	X				X	X	X	X	X
Moderate				X					
Low		X	X						

**VLEACH PARAMETER SENSITIVITY TO GROUNDWATER IMPACT**

	$K_{oc}$	$K_H$	$C_{sol}$	$D_{air}$	$q$	$\rho_b$	$\phi$	$\theta$	$f_{oc}$
High	X				X				X
Moderate						X		X	
Low		X	X	X			X		



**Figure 8.1** The effect of organic carbon partition coefficient on soil contaminant profile.



**Figure 8.2** The effect of organic carbon partition coefficient on soil contaminant loading to groundwater.

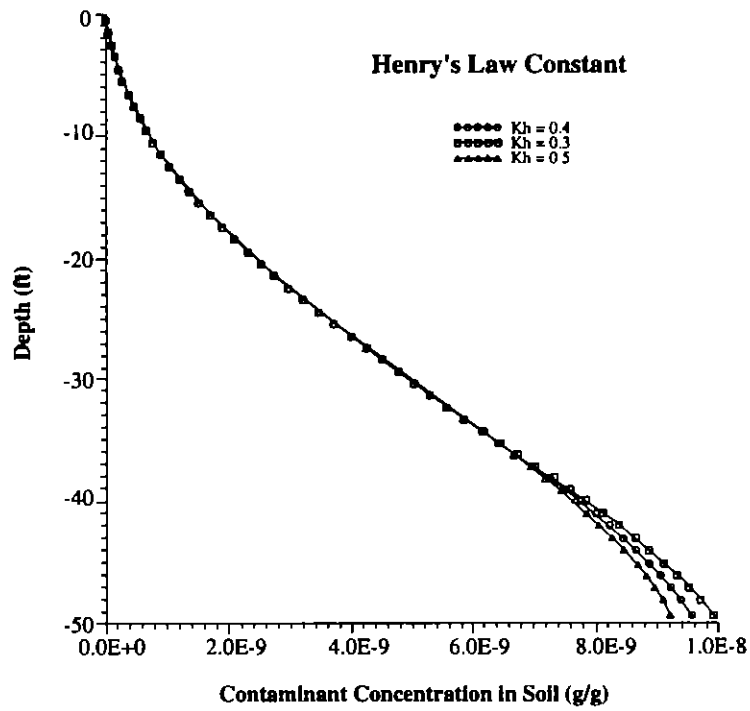


Figure 8.3 The effect of Henry's Law constant on soil contaminant profile.

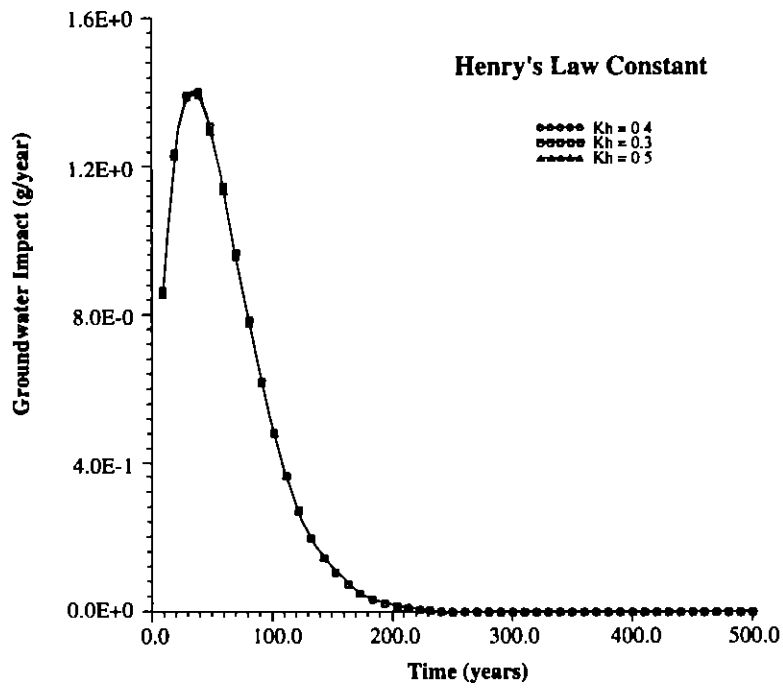
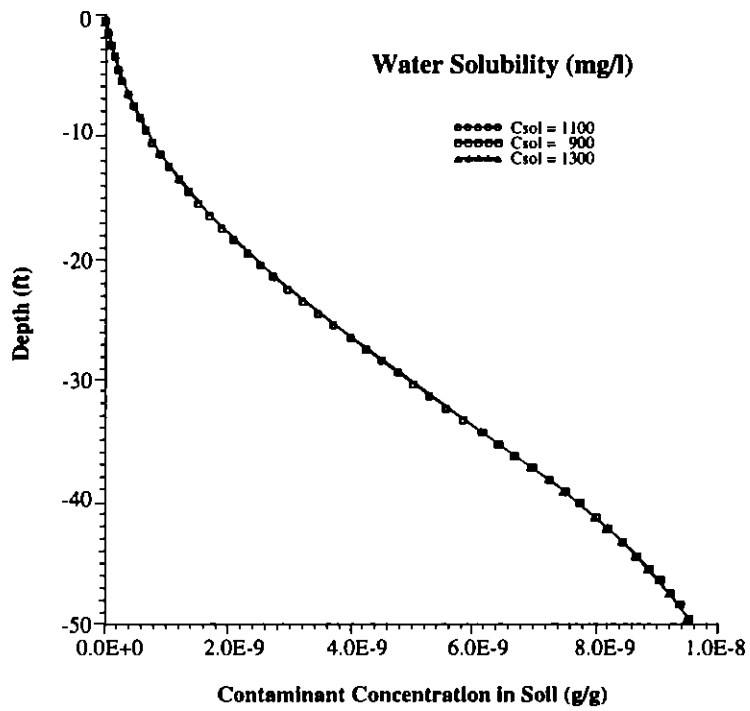
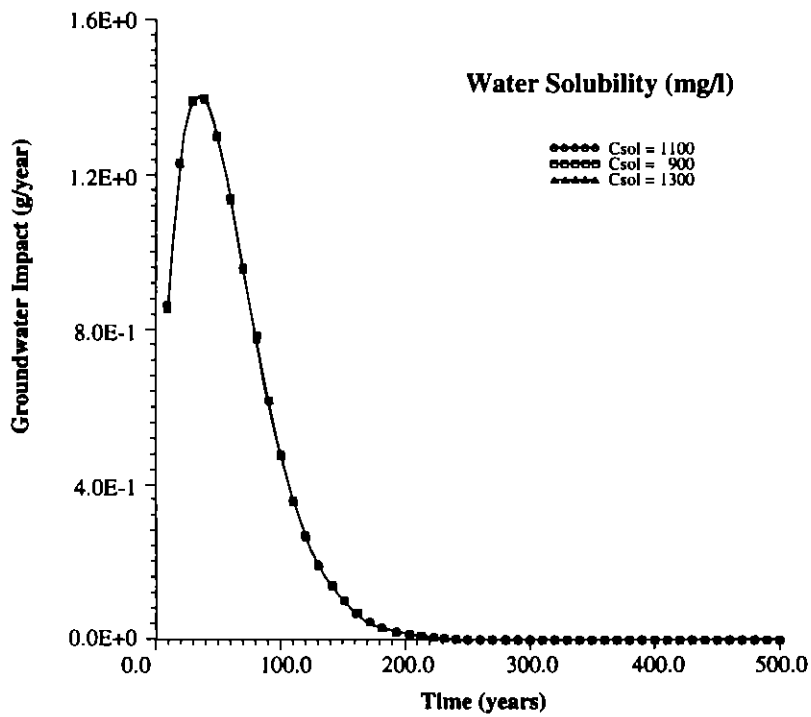


Figure 8.4 The effect of Henry's Law constant on contaminant loading to groundwater.



**Figure 8.5** *The effect of aqueous solubility on soil contaminant profile.*



**Figure 8.6** *The effect of aqueous solubility on contaminant loading to groundwater.*



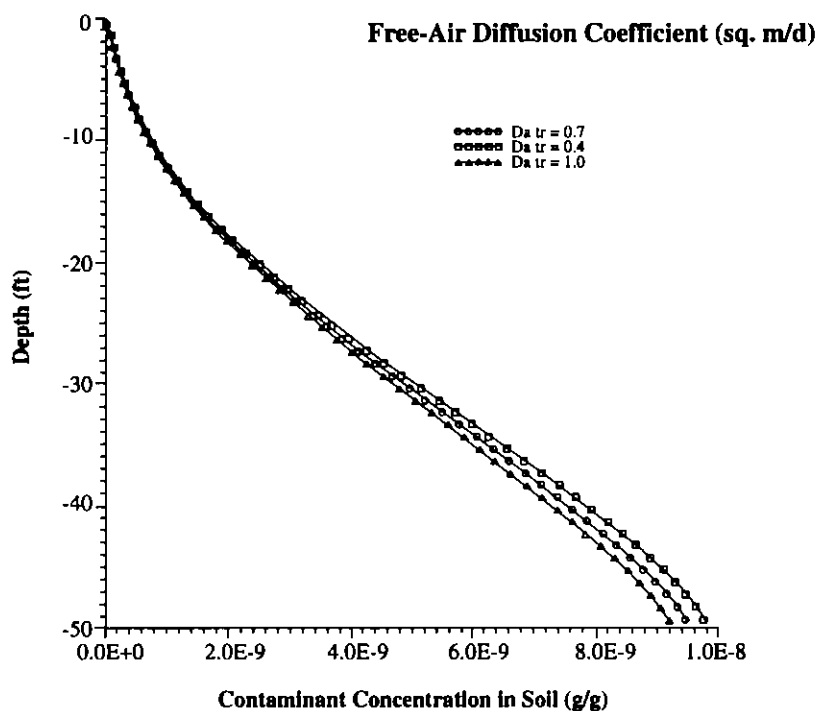


Figure 8.7 The effect of free-air diffusion coefficient on soil contaminant profile.

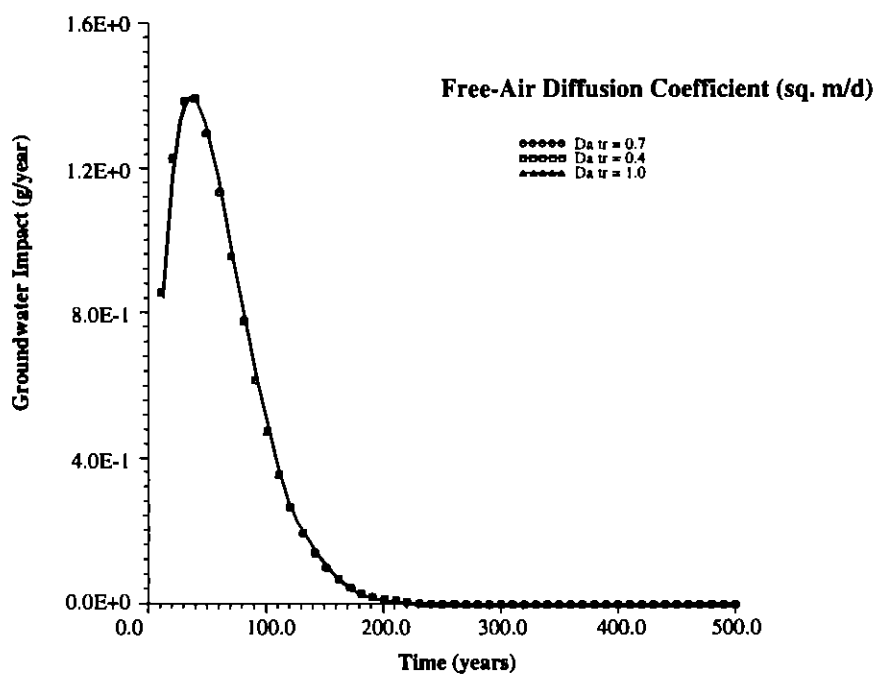
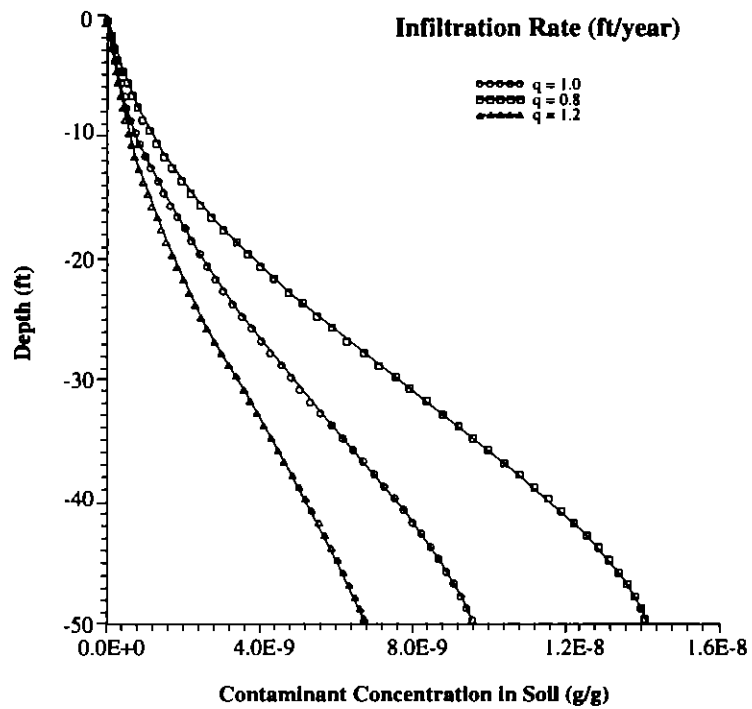
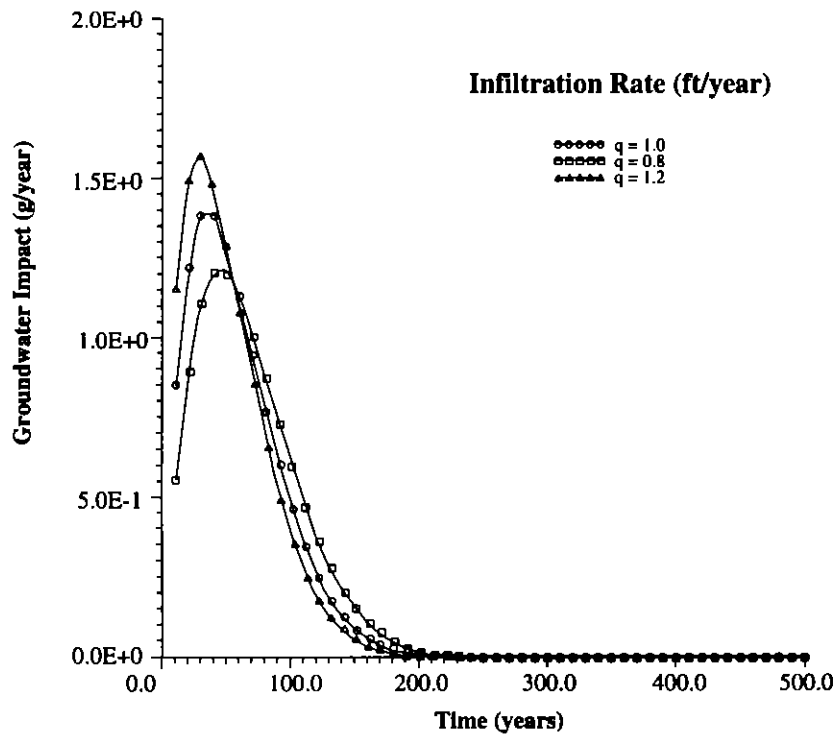


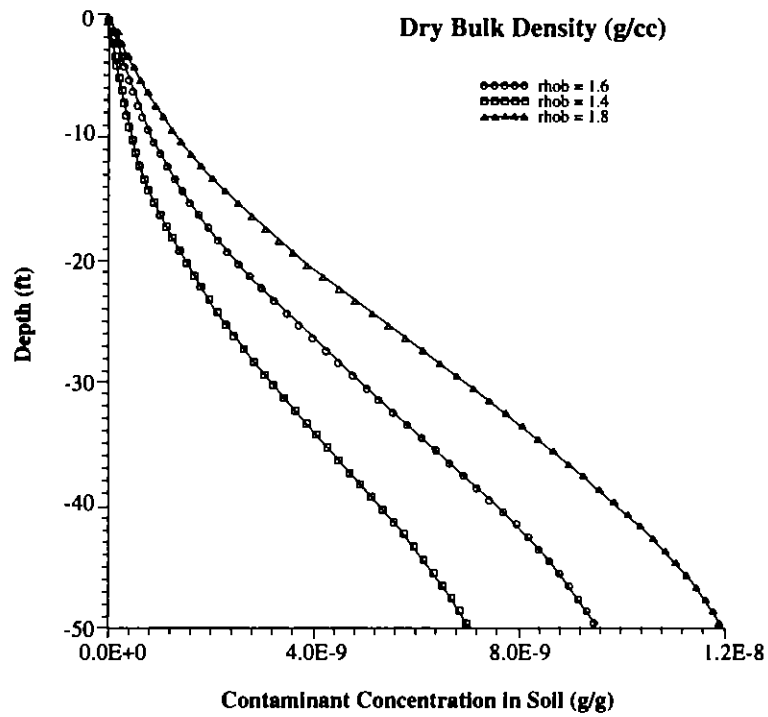
Figure 8.8 The effect of free-air diffusion coefficient on contaminant loading to groundwater.



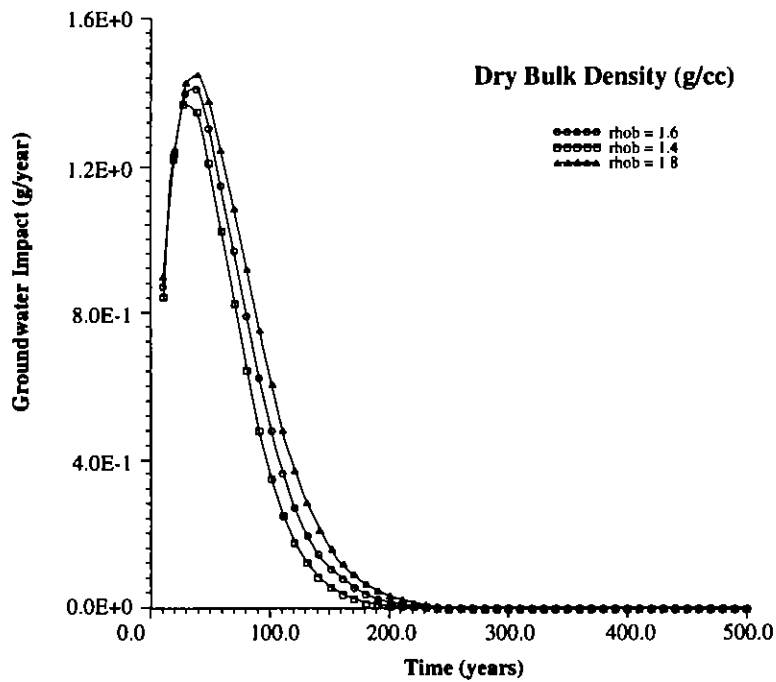
**Figure 8.9** The effect of infiltration rate on soil contaminant profile.



**Figure 8.10** The effect of infiltration rate on contaminant loading to groundwater.



**Figure 8.11** The effect of bulk density on soil contaminant profile.



**Figure 8.12** The effect of bulk density on contaminant loading to groundwater.

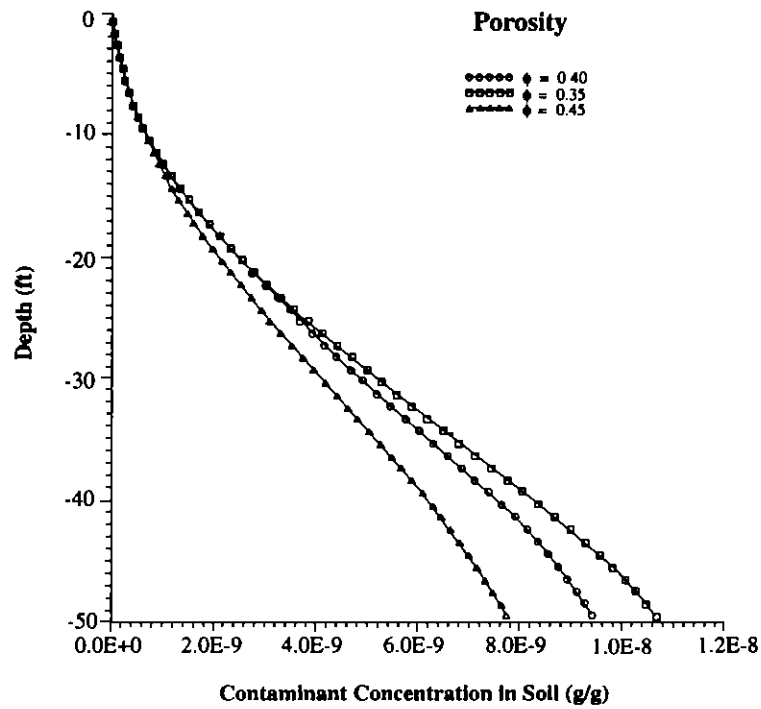


Figure 8.13 The effect of soil porosity on soil contaminant profile.

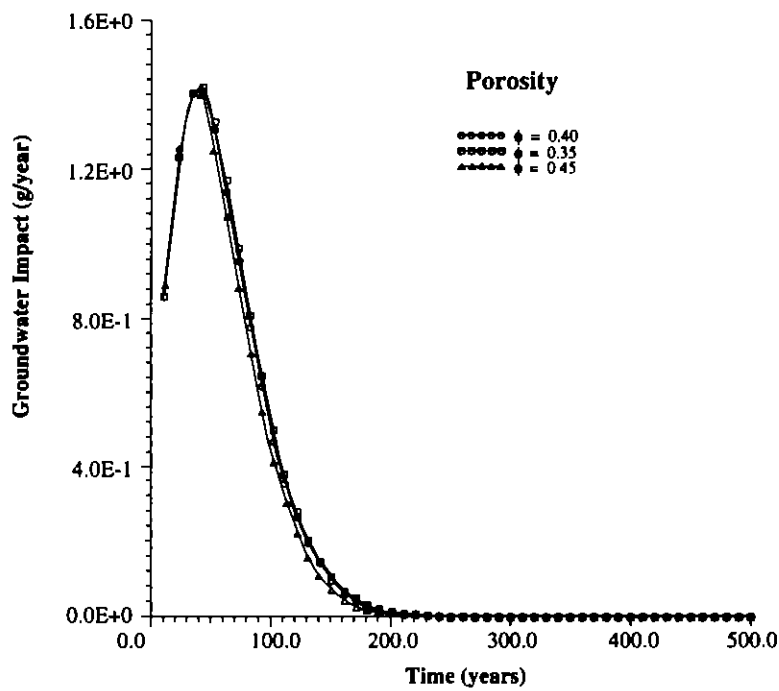


Figure 8.14 The effect of soil porosity on contaminant loading to groundwater.

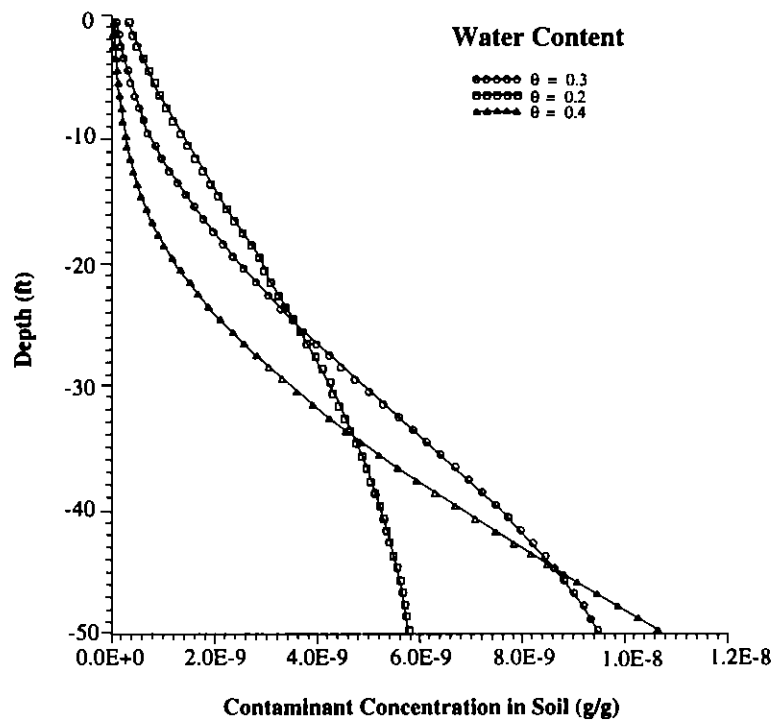


Figure 8.15 The effect of water content on soil contaminant profile.

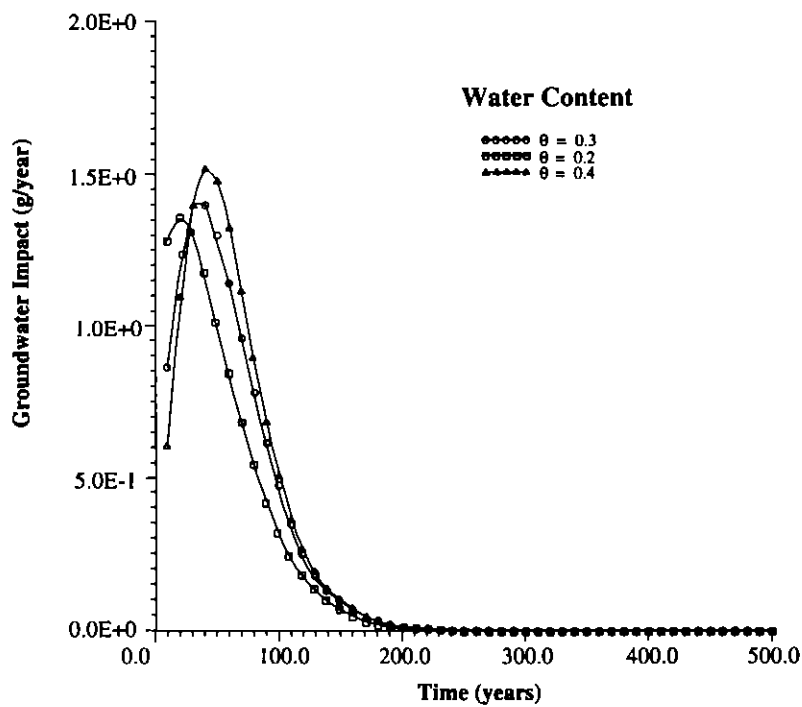
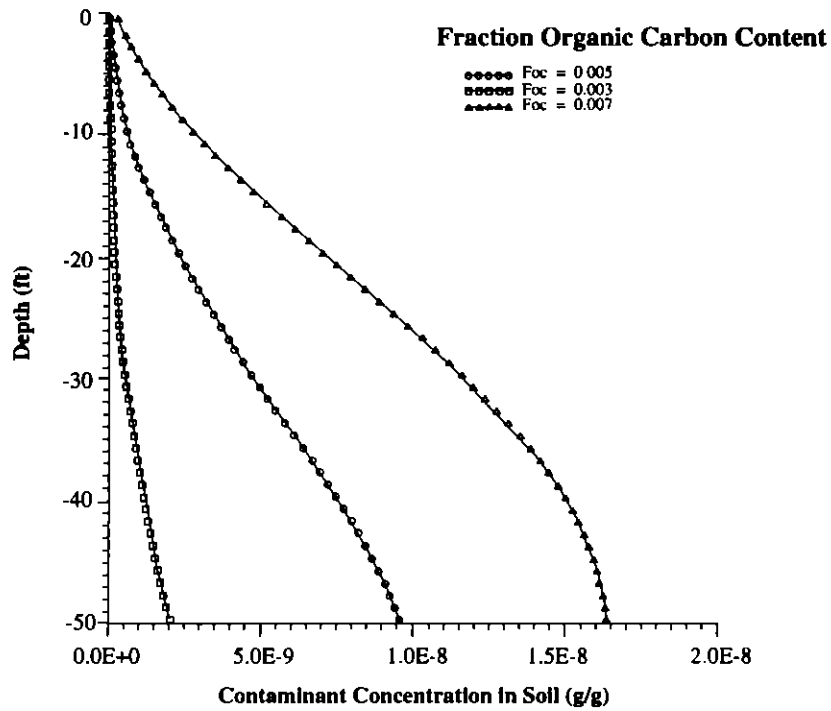
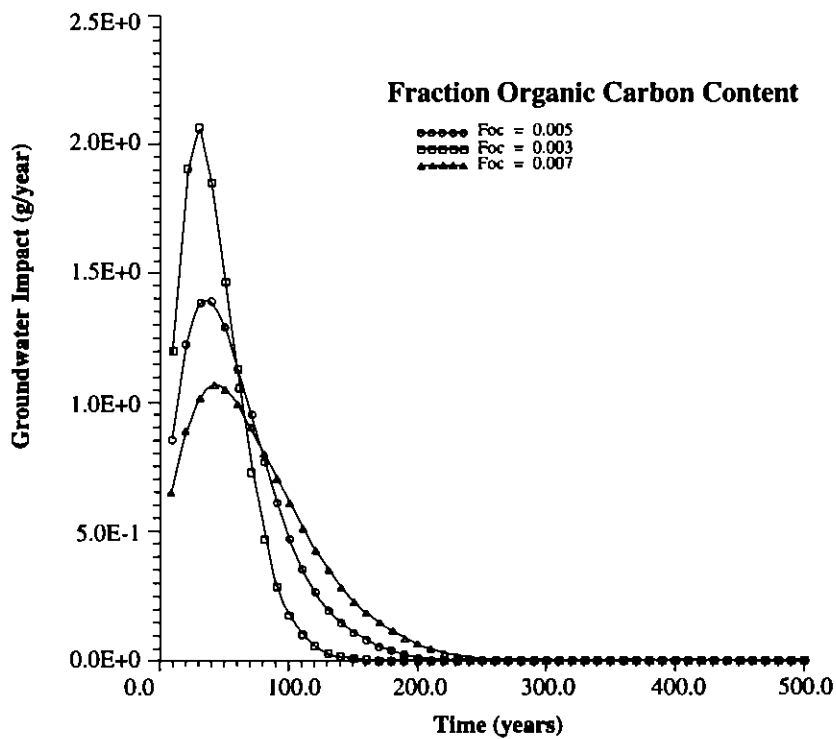


Figure 8.16 The effect of water content on contaminant loading to groundwater.



**Figure 8.17** The effect of fraction organic carbon on soil contaminant profile.



**Figure 8.18** The effect of fraction organic carbon on contaminant loading to groundwater.

## 9.0 SAMPLE PROBLEM

The following application of VLEACH is based on a hypothetical scenario. The scenario deals with evaluating TCE contamination of an aquifer that is located 50 feet below the soil surface. The soil is initially (prior to infiltration) contaminated with TCE, and the soil concentration along the depth is given as below:

DEPTH (ft)	TCE CONCENTRATION ( $\mu\text{g/kg}$ of soil)
1 - 20	100
20 - 30	50
30 - 40	10
40 - 50	0

The area of the contamination is 1000 square feet. The recharge rate to groundwater is 1 foot per year. The other soil, chemical, and computational parameters required for the execution of the model are presented below. These parameters are the same as that appearing in the input file, SAMPLE.INP.

### Model Parameters for the Sample Problem

#### Chemical Parameters

Organic Carbon Partition Coefficient ( $K_{oc}$ ) = 100 ml/g  
Henry's Law Constant ( $K_H$ ) = 0.4 (Dimensionless)  
Free Air Diffusion Coefficient ( $D_{air}$ ) = 0.7 m<sup>2</sup>/day  
Aqueous Solubility Limit ( $C_{sol}$ ) = 1100 mg/l

#### Soil Parameters

Bulk Density ( $\rho_b$ ) = 1.6 g/ml  
Porosity ( $\phi$ ) = 0.4  
Volumetric Water Content ( $\theta$ ) = 0.3  
Fraction Organic Carbon Content ( $f_{oc}$ ) = 0.005

#### Environmental Parameters

Recharge Rate ( $q$ ) = 1 ft/yr  
Concentration of TCE in Recharge Water = 0 mg/l  
Concentration of TCE in Atmospheric Air = 0 mg/l  
Concentration of TCE at the Water Table = 0 mg/l

#### Computational Parameters

Length of Simulation Period (STIME) = 500 years  
Time Step (DELTA) = 10 years  
Time Interval for Writing to .OUT file (PTIME) = 100 yrs  
Time Interval for Writing to .PRF file (PRTIME) = 250 yrs  
Size of a Cell (DELZ) = 1.0 ft  
Number of Cells (NCELL) = 50  
Number of Polygons (NPOLY) = 1

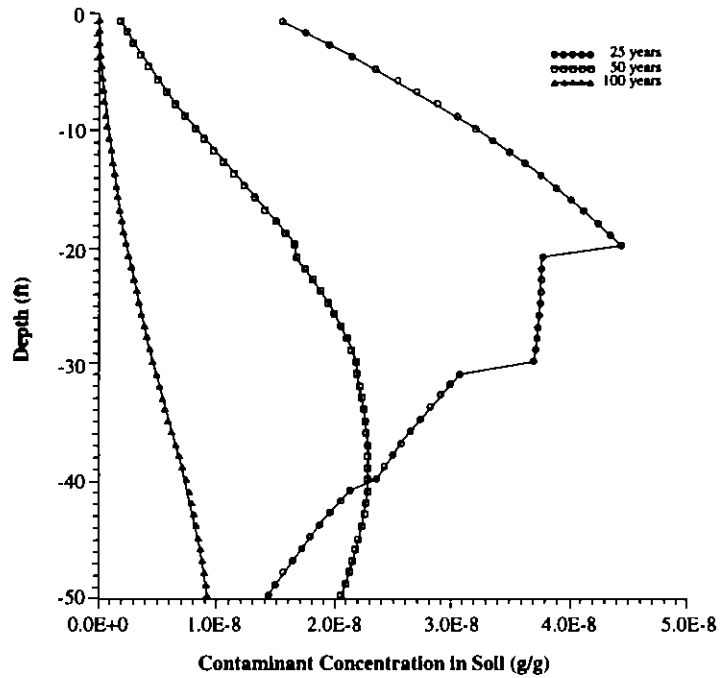
The output file results, SAMPLE.PRM, SAMPLE.OUT, and SAMPLE.PRF for the sample problem are presented in Appendix D. The essential parameter input information is echoed in SAMPLE.PRM. Each parameter is presented in terms of converted units (grams and feet) as well as the original units.

The output file, SAMPLE.OUT, provides all the essential results for every (PTIME) 100 years up to 500 years. This information includes mass per unit area of TCE remaining in each phase, change in total mass of TCE from previous printing time as well as starting time, an account for the change in mass due to various boundary fluxes (contribution of liquid-phase advection and gas-phase advection and diffusion on the boundaries), and the mass balance discrepancy. The file also provides important information on the amount of TCE released to groundwater (groundwater impact statement) in terms of grams per year, at different times (every PTIME step).

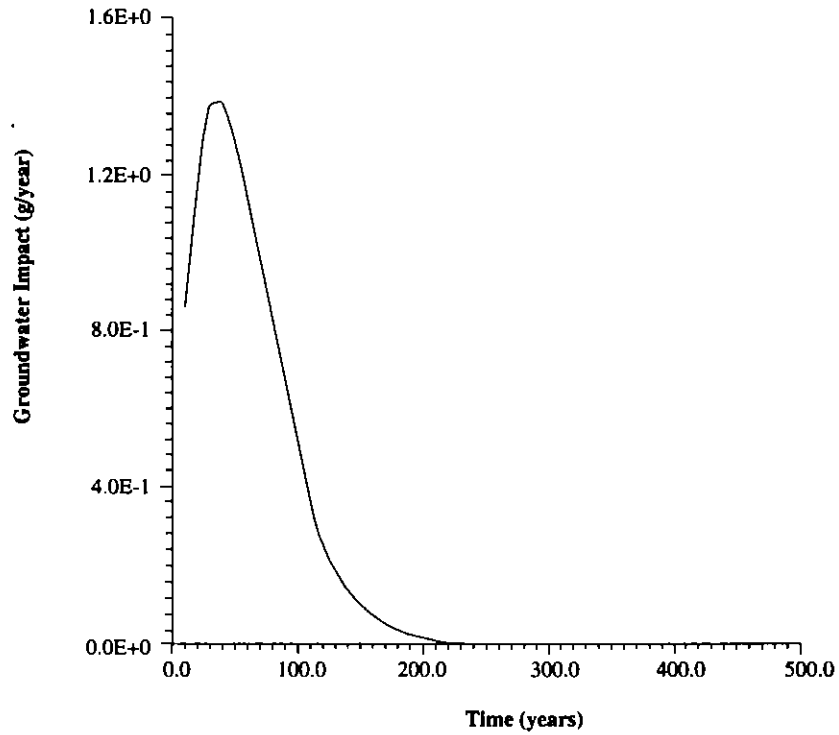
The SAMPLE.PRF file provides the variation of TCE concentration with soil depth in gas, liquid, and solid phases for each PRTIME step and for each polygon.

Figure 9.1 presents the concentration profile of TCE in soil for three different time values. The TCE level in the soil decreases from  $4.5\text{E}-08$  to  $1.0\text{E}-08$  with time due to leaching and volatilization. In addition the concentration of TCE becomes more evenly distributed with time. Figure 9.2 depicts the mass rate of TCE loading to groundwater as a function of time. The peak impact is approximately 1.4 g/year, and it occurs at about 50 years into the simulation.





**Figure 9.1** Predicted contaminant soil concentration profile at three different times.



**Figure 9.2** Predicted groundwater impact versus time.



## 10.0 REFERENCES

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**APPENDIX A**  
**SIMULATION PARAMETER INFORMATION**



## Properties of Volatile and Semi-Volatile Compounds

CHEMICAL	GROUP	TYPE	SOLUBILITY (mg/l)	HENRY'S CONSTANT (atm m <sup>3</sup> /mol)	HENRY'S CONSTANT (dimensionless)	DENSITY (g/cc)	LOG K <sub>ow</sub>	LOG K <sub>oc</sub> (cc/g)
Carbon Tetrachloride	Halogenated Volatile Organic	Liquid Solvent	8.00E+02	2.00E-02	8.13E-01	1.595	2.83	2.64
Chlorobenzene	Halogenated Volatile Organic	Liquid Solvent	4.90E+02	3.46E-03	1.41E-01	1.106	2.84	2.20
Chloroform	Halogenated Volatile Organic	Liquid Solvent	8.22E+03	3.75E-03	1.52E-01	1.485	1.97	1.64
Cis-1,2-dichloroethylene(d)	Halogenated Volatile Organic	Liquid Solvent	3.50E+03	7.50E-03	3.05E-01	1.284	1.86	1.50
1,1-Dichloroethane(a)	Halogenated Volatile Organic	Liquid Solvent	5.50E+03	5.70E-03	2.32E-01	1.175	1.79	1.48
1,2-Dichloroethane	Halogenated Volatile Organic	Liquid Solvent	8.69E+03	1.10E-03	4.47E-02	1.253	1.48	1.15
1,1-Dichloroethylene	Halogenated Volatile Organic	Liquid Solvent	4.00E+02	1.54E-01	6.26E+00	1.214	2.13	1.81
1,2-Dichloropropane(a)	Halogenated Volatile Organic	Liquid Solvent	2.70E+03	3.60E-03	1.46E-01	1.158	2.02	1.71
Ethylene Dibromide(g)	Halogenated Volatile Organic	Liquid Solvent	3.40E+03	3.18E-04	1.29E-02	2.172	1.76	1.45
Methylene Chloride	Halogenated Volatile Organic	Liquid Solvent	1.32E+04	2.57E-03	1.04E-01	1.325	1.25	0.94
1,1,2,2-Tetrachloroethane	Halogenated Volatile Organic	Liquid Solvent	2.90E+03	5.00E-04	2.03E-02	1.600	2.39	2.34
Tetrachloroethylene	Halogenated Volatile Organic	Liquid Solvent	1.50E+02	2.27E-02	9.23E-01	1.625	3.14	2.82
Trans-1,2-dichloroethylene(d)	Halogenated Volatile Organic	Liquid Solvent	6.30E+03	6.60E-03	2.68E-01	1.257	2.09	1.77
1,1,1-Trichloroethane	Halogenated Volatile Organic	Liquid Solvent	9.50E+02	2.76E-03	1.12E-01	1.325	2.49	2.18
1,1,2-Trichloroethane	Halogenated Volatile Organic	Liquid Solvent	4.50E+03	1.17E-03	4.76E-02	1.444	2.17	1.75
Trichloroethylene	Halogenated Volatile Organic	Liquid Solvent	1.00E+03	8.92E-03	3.63E-01	1.462	2.42	2.10
Chloroethane	Halogenated Volatile Organic	Gas	5.70E+03	1.10E-02	4.47E-01	0.941	1.43	1.17
Vinyl Chloride	Halogenated Volatile Organic	Gas	1.10E+03	6.95E-01	2.83E+01	0.912	0.60	0.91
Methyl Ethyl Ketone	Non-Halogenated Volatile Organic	Ketone/furan	2.68E+05	2.74E-05	1.11E-03	0.805	0.29	0.65
4-Methyl-2-Pentanone	Non-Halogenated Volatile Organic	Ketone/furan	1.90E+04	1.55E-04	6.30E-03	0.802	1.25	1.38
Tetrahydrofuran	Non-Halogenated Volatile Organic	Ketone/furan	3.00E+05	1.10E-04	4.47E-03	0.889	0.46	no data
Benzene	Non-Halogenated Volatile Organic	Aromatic	1.78E+03	5.43E-03	2.21E-01	0.877	2.13	1.81
Ethyl Benzene	Non-Halogenated Volatile Organic	Aromatic	1.52E+02	7.90E-03	3.21E-01	0.867	3.15	2.83
Styrene	Non-Halogenated Volatile Organic	Aromatic	3.00E+02	2.28E-03	9.27E-02	0.906	3.16	no data
Toluene	Non-Halogenated Volatile Organic	Aromatic	5.15E+02	6.61E-03	2.69E-01	0.867	2.73	2.41
m-Xylene	Non-Halogenated Volatile Organic	Aromatic	2.00E+02	6.91E-03	2.81E-01	0.864	3.20	2.84
o-Xylene	Non-Halogenated Volatile Organic	Aromatic	1.70E+02	4.94E-03	2.01E-01	0.880	3.12	2.84
p-Xylene	Non-Halogenated Volatile Organic	Aromatic	1.98E+02	7.01E-03	2.85E-01	0.861	3.15	2.84
Arochlor 1242	Halogenated Semi-volatile Organic	PCB	4.50E-01	3.40E-04	1.38E-02	1.385	5.58	5.00
Arochlor 1254	Halogenated Semi-volatile Organic	PCB	1.20E-02	2.80E-04	1.14E-02	1.538	6.03	no data
Arochlor 1260	Halogenated Semi-volatile Organic	PCB	2.70E-03	3.40E-04	1.38E-02	1.440	7.15	no data
Chlordane	Halogenated Semi-volatile Organic	Pesticide	5.60E-02	2.20E-04	8.94E-03	1.600	5.48	4.58
DDD	Halogenated Semi-volatile Organic	Pesticide	1.60E-01	7.96E-06	3.24E-04	1.385	5.56	5.38
DDE	Halogenated Semi-volatile Organic	Pesticide	4.00E-02	1.90E-04	7.72E-03	no data	5.69	5.41
DDT	Halogenated Semi-volatile Organic	Pesticide	3.10E-03	2.80E-05	1.14E-03	0.985	6.36	5.48
Dieldrin	Halogenated Semi-volatile Organic	Pesticide	1.86E-01	9.70E-06	3.94E-04	1.750	5.34	3.23
1,2 Dichlorobenzene	Halogenated Semi-volatile Organic	Chlorinated Benzene	1.00E+02	1.88E-03	7.64E-02	1.306	3.38	3.06
1,4 Dichlorobenzene	Halogenated Semi-volatile Organic	Chlorinated Benzene	8.00E+01	1.58E-03	6.42E-02	1.248	3.39	3.07

## Properties of Volatile and Semi-Volatile Compounds (continued)

CHEMICAL	GROUP	TYPE	SOLUBILITY (mg/l)	HENRY'S CONSTANT (atm m <sup>3</sup> /mol)	HENRY'S CONSTANT (dimensionless)	DENSITY (g/cc)	LOG K <sub>ow</sub>	LOG K <sub>oc</sub> (cc/g)
Pentachlorophenol(w)	Halogenated Semi-volatile Organic	Chlorinated Phenol	1.40E+01	2.80E-06	1.14E-04	1.978	5.12	4.80
2,3,4,6-Tetrachlorophenol	Halogenated Semi-volatile Organic	Chlorinated Phenol	1.00E+03	no data	no data	1.839	4.10	2.00
Acenaphthene	Non-Halogenated Semi-volatile Organic	PAH	3.88E+00	1.20E-03	4.88E-02	1.225	3.92	3.70
Anthracene	Non-Halogenated Semi-volatile Organic	PAH	7.50E-02	3.38E-05	1.37E-03	1.250	4.45	4.10
Benzo(a)anthracene	Non-Halogenated Semi-volatile Organic	PAH	1.40E-02	4.50E-06	1.83E-04	1.174	5.61	6.14
Benzo(a)pyrene	Non-Halogenated Semi-volatile Organic	PAH	3.80E-03	1.80E-05	7.32E-04	no data	6.06	6.74
Benzo(b)fluoranthene	Non-Halogenated Semi-volatile Organic	PAH	1.40E-02	1.19E-05	4.84E-04	no data	6.57	5.74
Benzo(ghi)perylene	Non-Halogenated Semi-volatile Organic	PAH	2.60E-04	5.34E-08	2.17E-06	no data	6.51	6.20
Benzo(k)fluoranthene	Non-Halogenated Semi-volatile Organic	PAH	4.30E-03	3.94E-05	1.60E-03	no data	6.06	5.74
Chrysene	Non-Halogenated Semi-volatile Organic	PAH	6.00E-03	1.05E-06	4.27E-05	1.274	5.61	5.30
Dibenz(a,h)anthracene	Non-Halogenated Semi-volatile Organic	PAH	2.50E-03	7.33E-08	2.98E-06	1.252	6.80	6.52
Fluorene	Non-Halogenated Semi-volatile Organic	PAH	2.63E-01	6.50E-06	2.64E-04	1.252	4.90	4.58
Indeno(1,2,3-cd)pyrene	Non-Halogenated Semi-volatile Organic	PAH	1.90E+00	7.65E-05	3.11E-03	1.203	4.18	3.90
2-Methyl Naphthalene	Non-Halogenated Semi-volatile Organic	PAH	5.30E-04	6.95E-08	2.83E-06	no data	6.50	6.20
Naphthalene	Non-Halogenated Semi-volatile Organic	PAH	2.54E+01	5.06E-02	2.06E+00	1.006	3.86	3.93
Phenanthrene	Non-Halogenated Semi-volatile Organic	PAH	3.10E+01	1.27E-03	5.16E-02	1.162	3.30	3.11
Pyrene	Non-Halogenated Semi-volatile Organic	PAH	1.18E+00	3.98E-05	1.62E-03	0.980	4.46	4.10
Phenol	Non-Halogenated Semi-volatile Organic	Non-chlorinated phenol	1.48E-01	1.20E-05	4.88E-04	1.271	4.88	4.58
2,4-Dinitrophenol	Non-Halogenated Semi-volatile Organic	Non-chlorinated phenol	8.40E+04	7.80E-07	3.17E-05	1.058	1.46	1.15
m-Cresol (e)	Non-Halogenated Semi-volatile Organic	Non-chlorinated phenol	6.00E+03	6.50E-10	2.64E-08	1.680	1.54	1.22
o-Cresol	Non-Halogenated Semi-volatile Organic	Non-chlorinated phenol	2.35E+04	3.80E-05	1.54E-03	1.038	1.96	1.43
p-Cresol	Non-Halogenated Semi-volatile Organic	Non-chlorinated phenol	3.10E+04	4.70E-05	1.91E-03	1.027	1.95	1.23
		Non-chlorinated phenol	2.40E+04	3.50E-04	1.42E-02	1.035	1.94	1.28



**APPENDIX B**

**POLYGON PARAMETER INFORMATION**



## Physical Properties of Soil

Soil Texture	Bulk Density (g/cc) (Jury, 1986)	Porosity		Percent Organic Matter (Rawls, 1983)
		(Li et al., 1976)	(Brakensiek, et al., 1981)	
		mean (std. deviation)	mean (std. deviation)	mean (std. deviation)
Sand	1.59 — 1.65	0.359 (0.056)	0.349 (0.107)	0.71 (1.06)
Loamy Sand		0.410 (0.068)	0.410 (0.065)	0.61 (1.16)
Sandy Loam	1.20 — 1.47	0.435 (0.086)	0.423 (0.076)	0.71 (1.29)
Silt Loam	1.47	0.485 (0.059)	0.484 (0.057)	0.58 (1.29)
Loam		0.451 (0.078)	0.452 (0.069)	0.52 (0.99)
Sandy Clay Loam		0.420 (0.059)	0.406 (0.049)	0.19 (0.34)
Silty Clay Loam		0.477 (0.057)	0.473 (0.046)	0.13 (0.42)
Clay Loam	1.20 — 1.36	0.476 (0.053)	0.476 (0.054)	0.10 (0.42)
Sandy Clay		0.426 (0.057)		0.38 (1.20)
Silty Clay	1.26	0.492 (0.064)		
Clay		0.482 (0.050)	0.475 (0.048)	0.38 (0.83)

•  $oc = om/1.724$ ; where  $oc$  = organic carbon content,  $cm$  = organic matter content (after Dragun, 1988)

## Soil Hydraulic Properties

Soil Texture	Saturated Hydraulic Conductivity (cm/hr)		Irreducible Water Content
	(Li et al., 1976)	(McCuen et al., 1981)	(Carsel and Parish, 1988)
Sand	63.36	24.6	0.045
Loamy Sand	56.28	78.84	0.057
Sandy Loam	12.48	17.93	0.065
Silt Loam	2.59	1.62	0.078
Loam	2.5	5.98	0.067
Sandy Clay Loam	2.27	4.72	0.1
Silty Clay Loam	0.61	1.07	0.089
Clay Loam	0.88	3.64	0.095
Sandy Clay	0.78	1.25	
Silty Clay	0.37	1.8	0.07
Clay	0.46	1.07	0.068

**APPENDIX C**  
**REFERENCE INFORMATION**



## REFERENCE INFORMATION

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4. USEPA, (1990) Subsurface Contamination Reference Guide, Office of Emergency and Remedial Response, EPA/540/2-90/011.
5. Verschueren, K. (1983), Handbook of Environmental Data on Organic Chemicals, 2nd Ed., Van Nostrand Reinhold Company, New York.





## **APPENDIX D**

### **OUTPUT RESULTS FROM THE SAMPLE PROBLEM**



# **Sample Problem - TCE contamination scenario**

Polygon I	1	10.0	500.	100.	250.			
		100.	.400	1100.	0.7			
		1000.	1.	1.0	1.6	0.40	.3	.005
		0.	0.	0.				
50y		100.0						
	1	20	100.0					
	21	30	50.0					
	31	40	10.0					
	41	50	0.0					

VLEACH  
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By:

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P.O. Box 1198  
Ada, OK 74820

Based on the original VLEACH (version 1.0)  
developed by CH<sub>2</sub>M Hill, Redding, California  
for USEPA Region IX

Sample Problem - TCE contamination scenario.

1 polygons.

Timestep = 10.00 years.

Simulation length = 500.00 years.

Printout every 100.00 years.

Vertical profile stored every 250.00 years.

Koc = 100.00 ml/g, 0.35314E-02 cu.ft./g

Kh = 0.40000 (dimensionless).

Aqueous solubility = 1100.0 mg/l, 31.149 g/cu.ft

Free air diffusion coefficient = .70000 sq. m/day, 2750.3 sq.ft./yr

Polygon 1

Polygon I

Polygon area = 1000.0 sq. ft.

50 cells, each cell 1.000 ft. thick.

Soil Properties:

Bulk density = 1.6000 g/ml, 45307. g/cu.ft.

Porosity = 0.4000 Volumetric water content = 0.3000

Organic carbon content = 0.00500000

Recharge Rate = 1.00000000 ft/yr

Conc. in recharge water = 0.00000 mg/l, 0.00000 g/cu.ft

Atmospheric concentration = 0.00000 mg/l, 0.00000 g/cu.ft

Water table has a fixed concentration of 0.00000 mg/l, 0.00000 g/

with respect to gas diffusion.

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Sample Problem - TCE contamination scenario

Polygon 1

At time = 0.00, total mass in vadose zone = 0.11779 g/sq.ft.  
Mass in gas phase = 0.41331E-02 g/sq.ft.  
Mass in liquid phase = 0.30999E-01 g/sq.ft.  
Mass sorbed = 0.82663E-01 g/sq.ft.

Polygon 1

At time = 100.00, total mass in vadose zone = 0.13162E-01 g/sq.ft.  
Mass in gas phase = 0.46184E-03 g/sq.ft.  
Mass in liquid phase = 0.34638E-02 g/sq.ft.  
Mass sorbed = 0.92368E-02 g/sq.ft.

Since last printout at time = 0.00

Change in Total Mass = -0.10463 g/sq.ft.  
Advection in from atmosphere = 0.00000 g/sq.ft.  
Advection in from water table = -0.97914E-01 g/sq.ft.  
Diffusion in from atmosphere = -0.34935E-02 g/sq.ft.  
Diffusion in from water table = -0.32245E-02 g/sq.ft.  
Total inflow at boundaries = -0.10463 g/sq.ft.  
Mass discrepancy = 0.29802E-07 g/sq.ft.

Since beginning of run at time = 0.0

Change in Total Mass = -0.10463 g/sq.ft.  
Advection in from atmosphere = 0.00000 g/sq.ft.  
Advection in from water table = -0.97914E-01 g/sq.ft.  
Diffusion in from atmosphere = -0.34935E-02 g/sq.ft.  
Diffusion in from water table = -0.32245E-02 g/sq.ft.  
Total inflow at boundaries = -0.10463 g/sq.ft.  
Mass discrepancy = 0.29802E-07 g/sq.ft.

Polygon 1

At time = 200.00, total mass in vadose zone = 0.36394E-03 g/sq.ft.  
Mass in gas phase = 0.12770E-04 g/sq.ft.  
Mass in liquid phase = 0.95774E-04 g/sq.ft.  
Mass sorbed = 0.25540E-03 g/sq.ft.

Since last printout at time = 100.00

Change in Total Mass = -0.12798E-01 g/sq.ft.  
     Advection in from atmosphere = 0.00000 g/sq.ft.  
     Advection in from water table = -0.12214E-01 g/sq.ft.  
     Diffusion in from atmosphere = -0.49549E-04 g/sq.ft.  
     Diffusion in from water table = -0.53490E-03 g/sq.ft.  
 Total inflow at boundaries = -0.12798E-01 g/sq.ft.  
 Mass discrepancy = 0.00000 g/sq.ft.

Since beginning of run at time = 0.0  
     Change in Total Mass = -0.11743 g/sq.ft.  
         Advection in from atmosphere = 0.00000 g/sq.ft.  
         Advection in from water table = -0.11013 g/sq.ft.  
         Diffusion in from atmosphere = -0.35430E-02 g/sq.ft.  
         Diffusion in from water table = -0.37594E-02 g/sq.ft.  
 Total inflow at boundaries = -0.11743 g/sq.ft.  
 Mass discrepancy = 0.37253E-07 g/sq.ft.

Polygon 1  
 At time = 300.00, total mass in vadose zone = 0.63882E-05 g/sq.ft.  
 Mass in gas phase = 0.22415E-06 g/sq.ft.  
 Mass in liquid phase = 0.16811E-05 g/sq.ft.  
 Mass sorbed = 0.44830E-05 g/sq.ft.

Since last printout at time = 200.00  
     Change in Total Mass = -0.35755E-03 g/sq.ft.  
         Advection in from atmosphere = 0.00000 g/sq.ft.  
         Advection in from water table = -0.34085E-03 g/sq.ft.  
         Diffusion in from atmosphere = -0.74487E-06 g/sq.ft.  
         Diffusion in from water table = -0.15963E-04 g/sq.ft.  
 Total inflow at boundaries = -0.35755E-03 g/sq.ft.  
 Mass discrepancy = 0.58208E-10 g/sq.ft.

Since beginning of run at time = 0.0  
     Change in Total Mass = -0.11779 g/sq.ft.  
         Advection in from atmosphere = 0.00000 g/sq.ft.  
         Advection in from water table = -0.11047 g/sq.ft.  
         Diffusion in from atmosphere = -0.35438E-02 g/sq.ft.  
         Diffusion in from water table = -0.37754E-02 g/sq.ft.  
 Total inflow at boundaries = -0.11779 g/sq.ft.  
 Mass discrepancy = 0.37253E-07 g/sq.ft.

Polygon 1  
 At time = 400.00, total mass in vadose zone = 0.96609E-07 g/sq.ft.  
 Mass in gas phase = 0.33898E-08 g/sq.ft.  
 Mass in liquid phase = 0.25424E-07 g/sq.ft.  
 Mass sorbed = 0.67796E-07 g/sq.ft.

Since last printout at time = 300.00  
     Change in Total Mass = -0.62916E-05 g/sq.ft.  
         Advection in from atmosphere = 0.00000 g/sq.ft.  
         Advection in from water table = -0.59935E-05 g/sq.ft.  
         Diffusion in from atmosphere = -0.10955E-07 g/sq.ft.  
         Diffusion in from water table = -0.28714E-06 g/sq.ft.  
 Total inflow at boundaries = -0.62916E-05 g/sq.ft.  
 Mass discrepancy = 0.00000 g/sq.ft.

Since beginning of run at time = 0.0  
     Change in Total Mass = -0.11779 g/sq.ft.

Advection in from atmosphere = 0.00000 g/sq.ft.  
 Advection in from water table = -0.11048 g/sq.ft.  
 Diffusion in from atmosphere = -0.35438E-02 g/sq.ft.  
 Diffusion in from water table = -0.37757E-02 g/sq.ft.  
 Total inflow at boundaries = -0.11779 g/sq.ft.  
 Mass discrepancy = 0.44703E-07g/sq.ft.

Polygon 1

At time = 500.00, total mass in vadose zone = 0.14074E-08g/sq.ft.  
 Mass in gas phase = 0.49384E-10 g/sq.ft.  
 Mass in liquid phase = 0.37038E-09 g/sq.ft.  
 Mass sorbed = 0.98767E-09 g/sq.ft.

Since last printout at time = 400.00

Change in Total Mass = -0.95202E-07g/sq.ft.  
 Advection in from atmosphere = 0.00000 g/sq.ft.  
 Advection in from water table = -0.90671E-07 g/sq.ft.  
 Diffusion in from atmosphere = -0.15912E-09 g/sq.ft.  
 Diffusion in from water table = -0.43723E-08 g/sq.ft.  
 Total inflow at boundaries = -0.95202E-07 g/sq.ft.  
 Mass discrepancy = -0.71054E-14g/sq.ft.

Since beginning of run at time = 0.0

Change in Total Mass = -0.11779 g/sq.ft.  
 Advection in from atmosphere = 0.00000 g/sq.ft.  
 Advection in from water table = -0.11048 g/sq.ft.  
 Diffusion in from atmosphere = -0.35438E-02 g/sq.ft.  
 Diffusion in from water table = -0.37757E-02 g/sq.ft.  
 Total inflow at boundaries = -0.11779 g/sq.ft.  
 Mass discrepancy = 0.44703E-07g/sq.ft.

GROUNDWATER IMPACT OF POLYGON 1

Time	Mass per area (g/sq.ft.)	Total Mass (g)
100.00	0.10114	101.14
200.00	0.12749E-01	12.749
300.00	0.35681E-03	0.35681
400.00	0.62807E-05	0.62807E-02
500.00	0.95043E-07	0.95043E-04
*****		
*****		

TOTAL GROUNDWATER IMPACT

Time (yr)	Mass (g)	Cumulative Mass (g)
100.00	101.14	101.14
200.00	12.749	113.89
300.00	0.35681	114.24
400.00	0.62807E-02	114.25
500.00	0.95043E-04	114.25

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Polygon 1

Time:

0.0000

Cell	Cgas(g/cu.ft)	Clig(g/cu.ft)	Csol(g/g)
1	0.15897E-02	0.39742E-02	0.70173E-07
2	0.15897E-02	0.39742E-02	0.70173E-07
3	0.15897E-02	0.39742E-02	0.70173E-07
4	0.15897E-02	0.39742E-02	0.70173E-07
5	0.15897E-02	0.39742E-02	0.70173E-07
6	0.15897E-02	0.39742E-02	0.70173E-07
7	0.15897E-02	0.39742E-02	0.70173E-07
8	0.15897E-02	0.39742E-02	0.70173E-07
9	0.15897E-02	0.39742E-02	0.70173E-07
10	0.15897E-02	0.39742E-02	0.70173E-07
11	0.15897E-02	0.39742E-02	0.70173E-07
12	0.15897E-02	0.39742E-02	0.70173E-07
13	0.15897E-02	0.39742E-02	0.70173E-07
14	0.15897E-02	0.39742E-02	0.70173E-07
15	0.15897E-02	0.39742E-02	0.70173E-07
16	0.15897E-02	0.39742E-02	0.70173E-07
17	0.15897E-02	0.39742E-02	0.70173E-07
18	0.15897E-02	0.39742E-02	0.70173E-07
19	0.15897E-02	0.39742E-02	0.70173E-07
20	0.15897E-02	0.39742E-02	0.70173E-07
21	0.79484E-03	0.19871E-02	0.35087E-07
22	0.79484E-03	0.19871E-02	0.35087E-07
23	0.79484E-03	0.19871E-02	0.35087E-07
24	0.79484E-03	0.19871E-02	0.35087E-07
25	0.79484E-03	0.19871E-02	0.35087E-07
26	0.79484E-03	0.19871E-02	0.35087E-07
27	0.79484E-03	0.19871E-02	0.35087E-07
28	0.79484E-03	0.19871E-02	0.35087E-07
29	0.79484E-03	0.19871E-02	0.35087E-07
30	0.79484E-03	0.19871E-02	0.35087E-07
31	0.15897E-03	0.39742E-03	0.70173E-08
32	0.15897E-03	0.39742E-03	0.70173E-08
33	0.15897E-03	0.39742E-03	0.70173E-08
34	0.15897E-03	0.39742E-03	0.70173E-08
35	0.15897E-03	0.39742E-03	0.70173E-08
36	0.15897E-03	0.39742E-03	0.70173E-08
37	0.15897E-03	0.39742E-03	0.70173E-08
38	0.15897E-03	0.39742E-03	0.70173E-08



39	0.15897E-03	0.39742E-03	0.70173E-08
40	0.15897E-03	0.39742E-03	0.70173E-08
41	0.00000	0.00000	0.00000
42	0.00000	0.00000	0.00000
43	0.00000	0.00000	0.00000
44	0.00000	0.00000	0.00000
45	0.00000	0.00000	0.00000
46	0.00000	0.00000	0.00000
47	0.00000	0.00000	0.00000
48	0.00000	0.00000	0.00000
49	0.00000	0.00000	0.00000
50	0.00000	0.00000	0.00000

Polygon I

Time:

Cell	250.000		
	Cgas(g/cu.ft)	Clq(g/cu.ft)	Csol(g/g)
1	0.74922E-09	0.18731E-08	0.33073E-13
2	0.16205E-08	0.40513E-08	0.71535E-13
3	0.26367E-08	0.65917E-08	0.11639E-12
4	0.38212E-08	0.95529E-08	0.16868E-12
5	0.52001E-08	0.13000E-07	0.22955E-12
6	0.68026E-08	0.17007E-07	0.30029E-12
7	0.86610E-08	0.21652E-07	0.38232E-12
8	0.10811E-07	0.27027E-07	0.47722E-12
9	0.13292E-07	0.33229E-07	0.58674E-12
10	0.16147E-07	0.40367E-07	0.71277E-12
11	0.19424E-07	0.48559E-07	0.85742E-12
12	0.23174E-07	0.57936E-07	0.10230E-11
13	0.27455E-07	0.68639E-07	0.12120E-11
14	0.32328E-07	0.80821E-07	0.14271E-11
15	0.37859E-07	0.94648E-07	0.16712E-11
16	0.44120E-07	0.11030E-06	0.19476E-11
17	0.51188E-07	0.12797E-06	0.22596E-11
18	0.59146E-07	0.14786E-06	0.26109E-11
19	0.68080E-07	0.17020E-06	0.30053E-11
20	0.78086E-07	0.19522E-06	0.34470E-11
21	0.89258E-07	0.22315E-06	0.39401E-11
22	0.10170E-06	0.25426E-06	0.44895E-11
23	0.11553E-06	0.28882E-06	0.50997E-11
24	0.13085E-06	0.32712E-06	0.57760E-11
25	0.14778E-06	0.36944E-06	0.65233E-11
26	0.16644E-06	0.41611E-06	0.73473E-11
27	0.18697E-06	0.46742E-06	0.82534E-11
28	0.20948E-06	0.52371E-06	0.92473E-11
29	0.23412E-06	0.58530E-06	0.10335E-10
30	0.26101E-06	0.65253E-06	0.11522E-10
31	0.29028E-06	0.72571E-06	0.12814E-10
32	0.32208E-06	0.80519E-06	0.14217E-10
33	0.35652E-06	0.89129E-06	0.15738E-10
34	0.39373E-06	0.98432E-06	0.17380E-10
35	0.43383E-06	0.10846E-05	0.19151E-10
36	0.47695E-06	0.11924E-05	0.21054E-10
37	0.52318E-06	0.13079E-05	0.23095E-10
38	0.57262E-06	0.14315E-05	0.25277E-10
39	0.62534E-06	0.15633E-05	0.27604E-10
40	0.68140E-06	0.17035E-05	0.30079E-10
41	0.74086E-06	0.18521E-05	0.32704E-10
42	0.80371E-06	0.20093E-05	0.35478E-10
43	0.86996E-06	0.21749E-05	0.38403E-10
44	0.93956E-06	0.23489E-05	0.41475E-10

45	0.10124E-05	0.25311E-05	0.44692E-10
46	0.10884E-05	0.27211E-05	0.48047E-10
47	0.11674E-05	0.29185E-05	0.51533E-10
48	0.12491E-05	0.31228E-05	0.55140E-10
49	0.13333E-05	0.33332E-05	0.58855E-10
50	0.14195E-05	0.35488E-05	0.62663E-10

Polygon I

Time:	500.000		
Cell	Cgas(g/cu.ft)	Clig(g/cu.ft)	Csol(g/g)
1	0.19048E-13	0.47620E-13	0.84083E-18
2	0.41161E-13	0.10290E-12	0.18170E-17
3	0.66829E-13	0.16707E-12	0.29500E-17
4	0.96593E-13	0.24148E-12	0.42639E-17
5	0.13105E-12	0.32763E-12	0.57851E-17
6	0.17088E-12	0.42719E-12	0.75430E-17
7	0.21680E-12	0.54200E-12	0.95702E-17
8	0.26964E-12	0.67410E-12	0.11903E-16
9	0.33030E-12	0.82575E-12	0.14581E-16
10	0.39979E-12	0.99946E-12	0.17648E-16
11	0.47920E-12	0.11980E-11	0.21153E-16
12	0.56975E-12	0.14244E-11	0.25150E-16
13	0.67279E-12	0.16820E-11	0.29699E-16
14	0.78979E-12	0.19745E-11	0.34864E-16
15	0.92238E-12	0.23060E-11	0.40717E-16
16	0.10723E-11	0.26808E-11	0.47336E-16
17	0.12416E-11	0.31040E-11	0.54809E-16
18	0.14323E-11	0.35809E-11	0.63228E-16
19	0.16469E-11	0.41172E-11	0.72698E-16
20	0.18877E-11	0.47193E-11	0.83330E-16
21	0.21577E-11	0.53942E-11	0.95247E-16
22	0.24598E-11	0.61494E-11	0.10858E-15
23	0.27973E-11	0.69931E-11	0.12348E-15
24	0.31737E-11	0.79341E-11	0.14010E-15
25	0.35928E-11	0.89821E-11	0.15860E-15
26	0.40589E-11	0.10147E-10	0.17917E-15
27	0.45762E-11	0.11441E-10	0.20201E-15
28	0.51497E-11	0.12874E-10	0.22732E-15
29	0.57844E-11	0.14461E-10	0.25534E-15
30	0.64857E-11	0.16214E-10	0.28630E-15
31	0.72595E-11	0.18149E-10	0.32046E-15
32	0.81118E-11	0.20280E-10	0.35808E-15
33	0.90494E-11	0.22623E-10	0.39947E-15
34	0.10079E-10	0.25197E-10	0.44491E-15
35	0.11208E-10	0.28019E-10	0.49474E-15
36	0.12443E-10	0.31108E-10	0.54927E-15
37	0.13793E-10	0.34482E-10	0.60887E-15
38	0.15266E-10	0.38164E-10	0.67387E-15
39	0.16869E-10	0.42173E-10	0.74465E-15
40	0.18612E-10	0.46530E-10	0.82159E-15
41	0.20503E-10	0.51257E-10	0.90505E-15
42	0.22550E-10	0.56374E-10	0.99541E-15
43	0.24761E-10	0.61904E-10	0.10930E-14
44	0.27146E-10	0.67865E-10	0.11983E-14
45	0.29711E-10	0.74278E-10	0.13115E-14
46	0.32464E-10	0.81159E-10	0.14330E-14
47	0.35410E-10	0.88524E-10	0.15631E-14
48	0.38554E-10	0.96386E-10	0.17019E-14
49	0.41901E-10	0.10475E-09	0.18497E-14
50	0.45453E-10	0.11363E-09	0.20064E-14

**APPENDIX E**  
**MODEL DATA SHEET**

## VLEACH MODEL DATA SHEET

Modeler(s): \_\_\_\_\_  
Date: \_\_\_\_\_  
Chemical Name: \_\_\_\_\_

### Simulation Data

Title: \_\_\_\_\_  
Number of Polygons: \_\_\_\_\_  
Timestep: \_\_\_\_\_ (years)  
Simulation Time: \_\_\_\_\_ (years)  
Output Time Interval: \_\_\_\_\_ (years)  
Profile Time Interval: \_\_\_\_\_ (years)  
Organic Carbon Distribution  
Coefficient: \_\_\_\_\_ (ml/g)  
Henry's Constant: \_\_\_\_\_  
Water Solubility: \_\_\_\_\_ (mg/L)  
Free Air Diffusion  
Coefficient: \_\_\_\_\_ (m<sup>2</sup>/day)

### Polygon Data

Title: \_\_\_\_\_  
Area: \_\_\_\_\_ (feet<sup>2</sup>)  
Vertical Cell  
Dimension: \_\_\_\_\_ (feet)  
Recharge Rate: \_\_\_\_\_ (feet/year)  
Dry Bulk Density: \_\_\_\_\_ (g/cm<sup>3</sup>)  
Effective Porosity: \_\_\_\_\_  
Volumetric Water  
Content: \_\_\_\_\_  
Soil Organic Carbon  
Content: \_\_\_\_\_  
Concentration of  
Recharge Water: \_\_\_\_\_ (mg/L)  
Upper Boundary Condition: \_\_\_\_\_ (mg/L)  
Lower Boundary Condition: \_\_\_\_\_ (mg/L)  
Cell Number: \_\_\_\_\_  
Initial Contaminant  
Concentration in Cells: \_\_\_\_\_ (µg/kg)

# **HYDROGEOLOGIC SETTING, HYDRAULIC PROPERTIES, AND GROUND-WATER FLOW AT THE O-FIELD AREA OF ABERDEEN PROVING GROUND, MARYLAND**

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**U.S. GEOLOGICAL SURVEY**

**Water-Resources Investigations Report 95-4248**



Prepared in cooperation with the

**U.S. ARMY ABERDEEN PROVING GROUND SUPPORT ACTIVITY  
ENVIRONMENTAL CONSERVATION AND RESTORATION DIVISION  
ABERDEEN PROVING GROUND, MARYLAND**

The text of this article has been approved for public release and unlimited distribution by the U.S. Army--distribution number 1424-A-3

## CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

	<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
<b>LENGTH</b>			
inch (in.)		2.54	centimeter
foot (ft)		0.3048	meter
mile (mi)		1.609	kilometer
<b>AREA</b>			
acre	4,047		square meter
acre		0.4047	hectare
square foot (ft <sup>2</sup> )		0.09294	square meter
square mile (mi <sup>2</sup> )		259.0	hectare
square mile (mi <sup>2</sup> )		2.590	square kilometer
<b>FLOW</b>			
inch per year (in/yr)		0.02540	meter per year
foot per second (ft/s)		0.3048	meter per second
foot per day (ft/d)		0.3048	meter per day
cubic foot per second (ft <sup>3</sup> /s)		0.02832	cubic meter per second
gallon per minute (gal/min)		0.06308	liter per second
gallon per day (gal/d)		0.003785	cubic meter per day
million gallons per day (Mgal/d)		0.04381	cubic meters per second
million gallons per day per square mile [(Mgal/d)/mi <sup>2</sup> ]	1,460		cubic meter per day per square kilometer
<b>TEMPERATURE</b>			
degree Fahrenheit (°F)		°C = 5/9x (°F-32)	degree Celsius
<b>HYDRAULIC CONDUCTIVITY</b>			
foot per day (ft/d)		0.3048	meter per day
<b>TRANSMISSIVITY</b>			
cubic foot per day per square foot times foot of aquifer thickness [(ft <sup>3</sup> /d)/ft <sup>2</sup> ]/ft		0.09290	cubic meter per day per square meter times meter of aquifer thickness

**Sea Level:** In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level datum of 1929.

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Towson, Maryland

1996

**U.S. DEPARTMENT OF THE INTERIOR**

**BRUCE BABBITT, Secretary**

**U.S. GEOLOGICAL SURVEY**

**Gordon P. Eaton, Director**

---

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*By William S. L. Banks, Barry S. Smith, and Colleen A. Donnelly*

## **ABSTRACT**

The U.S. Army disposed chemical agents, laboratory materials, and unexploded ordnance at O-Field in the Edgewood Area of Aberdeen Proving Ground, Maryland, from before World War II until at least the 1950's. Soil, ground water, surface water, and wetland sediments in the O-Field area were contaminated from the disposal activity. A ground-water-flow model of the O-Field area was constructed by the U.S. Geological Survey (USGS) in 1989 to simulate flow in the central and southern part of Gunpowder Neck. The USGS began an additional study of the contamination in the O-Field area in cooperation with the U.S. Army in 1990 to (1) further define the hydrogeologic framework of the O-Field area, (2) characterize the hydraulic properties of the aquifers and confining unit, and (3) define ground-water flow paths at O-Field on the basis of the current data and simulations of ground-water flow.

A water-table aquifer, an upper confining unit, and an upper confined aquifer comprise the shallow ground-water system of the O-Field area. A lower confining unit, through which ground-water movement is negligible, is considered a lower boundary to the shallow system. These units are all part of the Pleistocene Talbot Formation.

The model developed in the previous study was redesigned using the data collected during this study and emphasized New O-Field. The current steady-state model was calibrated to water levels of June 1993. The rate of ground-water flow calculated by the model was approximately 0.48 feet per day and the rate determined from chlorofluorocarbon dates was approximately 0.39 feet per day.

## INTRODUCTION

The Edgewood Area of Aberdeen Proving Ground (APG) has been the primary chemical warfare research and development center for the U.S. Army since 1917. APG includes approximately 145 mi<sup>2</sup> and is split between the Edgewood Area and the Aberdeen Area, two peninsulas in the northern part of the Chesapeake Bay (fig. 1). During the past 50 years, release of hazardous materials into the environment resulted from disposal of chemical agents, contaminated materials, and unexploded ordnance at O-Field in the Edgewood Area of APG, Maryland (fig. 1). Soil, surface water, ground water, and wetland sediments at O-Field were contaminated from the disposal activity. O-Field is approximately 1 mi<sup>2</sup> in area and about 2.7 mi north of the southern tip of Gunpowder Neck. O-Field is divided into Old O-Field, the northernmost site, and New O-Field, which is about 1,500 ft south of Old O-Field (fig. 2).

### Background

The U.S. Geological Survey (USGS), in cooperation with the U.S. Army, began to study O-Field in 1990 as part of the remedial investigation and feasibility study required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The study was directed through the Directorate of Health, Safety, and Environment (DSHE) of APG. In 1992, DSHE also installed wells to pump and treat contaminated ground water at Old O-Field. Since 1990, the USGS has been working with the U.S. Army and ICF Kaiser Engineers to study the hydrogeologic framework and ground-water flow in the O-Field area.

Disposal activity may have begun at the Old O-Field site as early as the 1930's, with most of the disposal activities occurring during and after World War II. Disposal was accomplished by burial and burning in unlined trenches. Explosions in some trenches in late 1949 ejected ordnance and contaminants over the Old O-Field site and into Watson Creek. In an effort to decontaminate the site, 1,000 barrels of decontamination agent

noncorrosive (DANC) were dispersed on and around the site. An effort to clean up the site in the early 1950's involved open-pit burning using fuel oil to burn chemical ordnance and debris (Yon and others, 1978). A fire at Old O-Field, probably from ignition of a white phosphorous munition, was reported as late as 1984 (Vroblesky and others, 1989).

Disposal began at New O-Field in 1950 and continued until the 1970's. A common method of disposal involved placing ordnance, dunnage, and fuel oil in an open pit and igniting the mixture. Occasionally, large fires outside the designated pit resulted from the explosion of rounds of ammunition. Chemical-warfare agents, unexploded ordnance, contaminated laboratory equipment, and dead animals were buried in trenches at New O-Field from 1950 to 1961 (Yon and others, 1978). Some contaminants, including dead animals, were later removed. Some of the disposal pits at both Old and New O-Fields remain and, as late as 1994, wastes were observed in collapsing and eroding trenches at Old O-Field (ICF Kaiser Engineers, 1994).

In 1978, the U.S. Army detected arsenic and chlorinated organic solvents in ground water at Old O-Field (Nemeth and others, 1983). In 1984, arsenic, cadmium, iron, and volatile organic compounds were confirmed in the ground water at Old O-Field by the U.S. Army Toxics and Hazardous Materials Agency (USATHAMA). In 1985, the U.S. Army Environmental Hygiene Agency found concentrations of organic and inorganic contaminants in Watson Creek. In 1989, arsenic and cadmium were reported above the U.S. Environmental Protection Agency's (USEPA) maximum contaminant levels (MCL) in the water-table aquifer at Old O-Field (Vroblesky and others, 1989). Benzene, carbon tetrachloride, trichloroethylene, and vinyl chloride also were present. Concentrations of numerous other inorganic and organic contaminants (some above MCL's) also were reported by Vroblesky and others (1989) in the shallow aquifers of Old O-Field as well as in the sediment and surface water of Watson Creek.

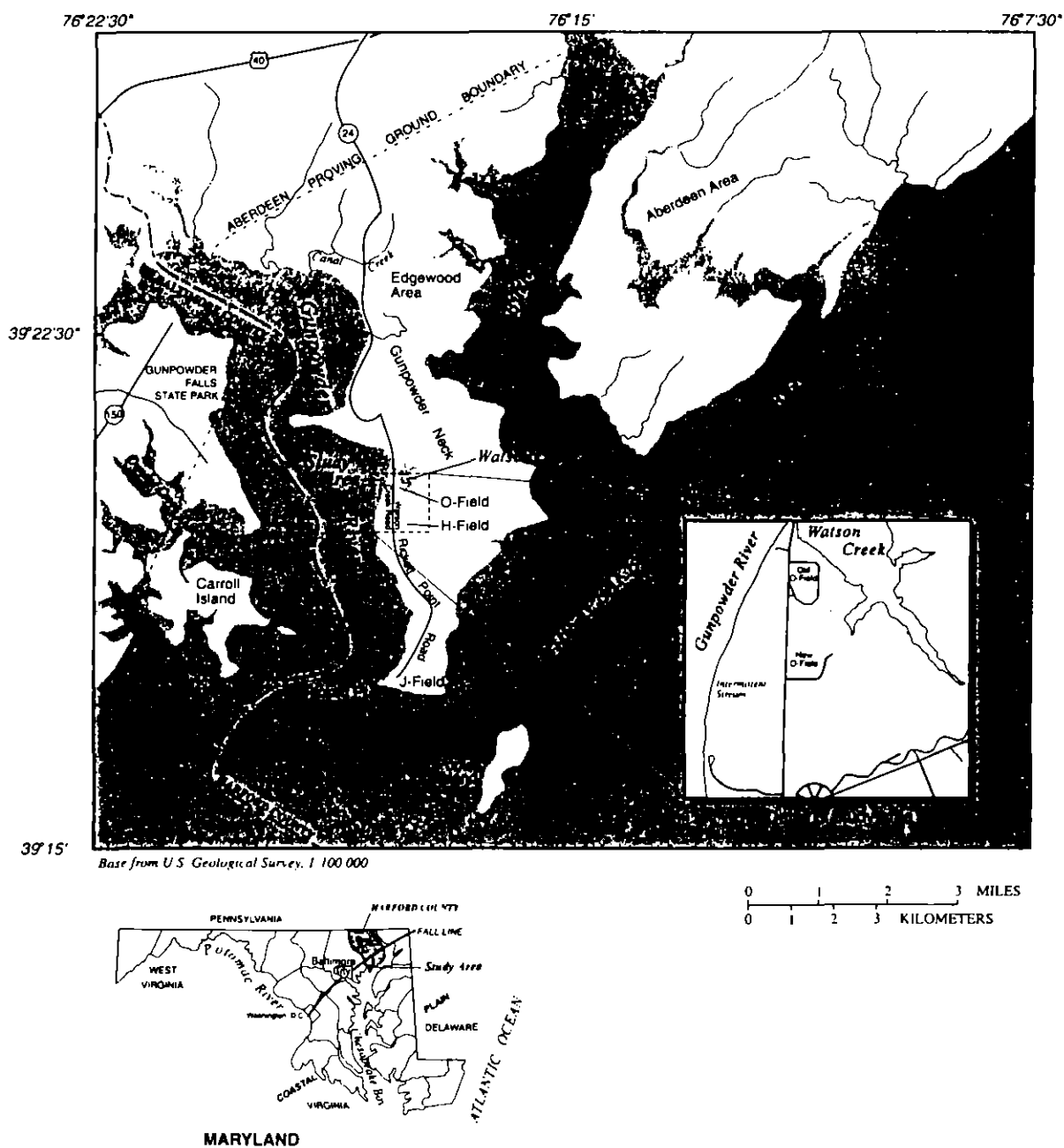


Figure 1. Location of the O-Field area, Aberdeen Proving Ground, Maryland.

(ICF Kaiser Engineers, 1994). The sediments range in color from black to gray or greenish gray (Vroblesky and others, 1989).

The clay content of the upper confining unit is greater beneath Old O-Field than beneath New O-Field. In places, particularly at New O-Field where the upper confining unit contains a large proportion of sand, the upper confining unit is difficult to distinguish from the water-table aquifer.

The top of the upper confining unit is about 4 ft below sea level near Watson Creek Road and about 12 to 16 ft below sea level beneath Watson Creek (fig. 5). The top of the unit slopes to the east beneath Old and New O-Fields; however, the surface undulates, indicating that it has been partially eroded in places by streams or that the

thickness of the unit varied at the time of deposition.

According to Vroblesky and others (1989), undisturbed parts of the upper confining unit were probably thicker beneath Old O-Field than beneath New O-Field. Furthermore, trenches may have been dug through the upper confining unit in many places at both Old and New O-Fields. In addition, data from borings at New O-Field showed that the upper confining unit is considerably thinner beneath New O-Field. The upper confining unit ranges from approximately 1 to 4 ft thick at Old O-Field, but in most of New O-Field, it is approximately 1 ft thick or less (fig. 6). The water-table aquifer could, therefore, be hydraulically connected to or poorly separated from the upper confined aquifer in some places.

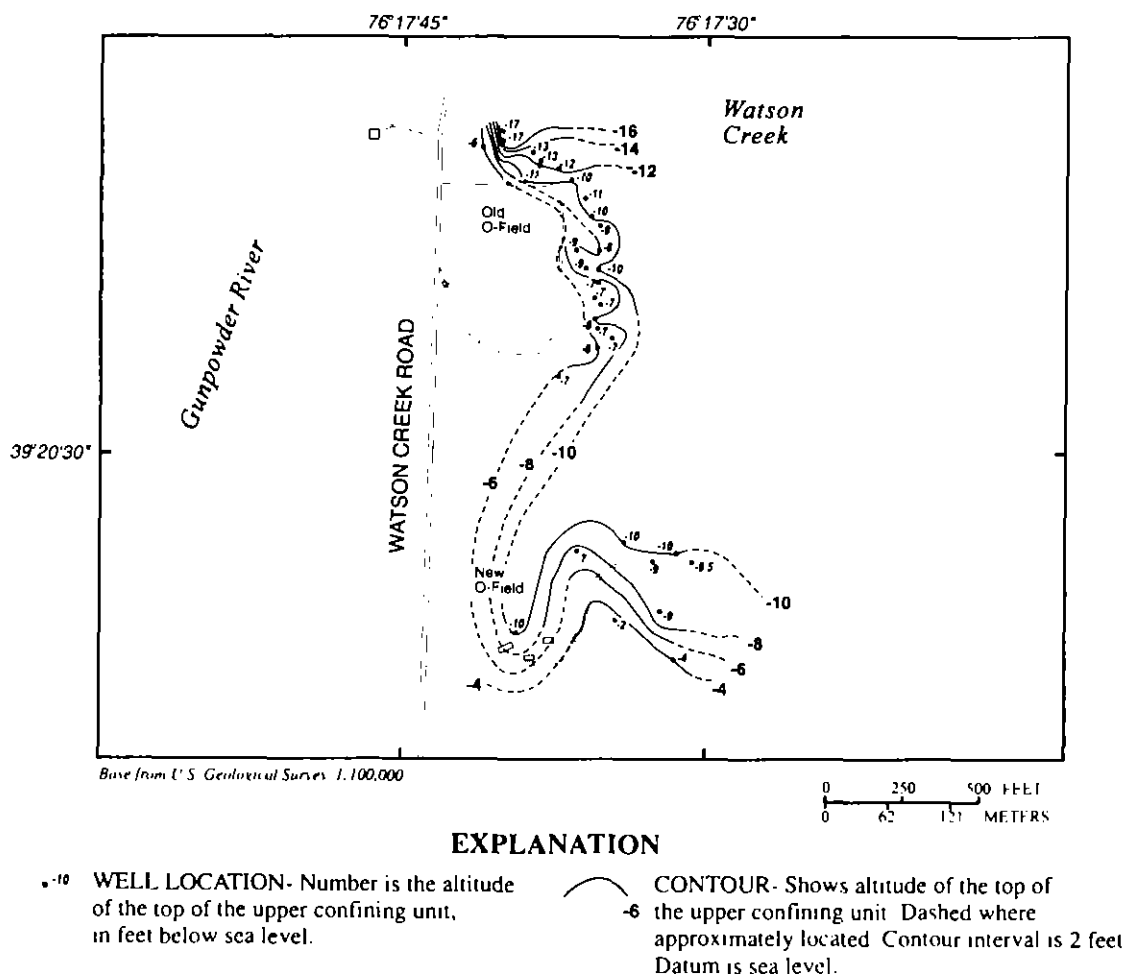


Figure 5. Altitude of the top of the upper confining unit at O-Field.

In 1986, the USEPA issued a Resource Conservation and Recovery Act (RCRA) Corrective Action permit to the U. S. Army for APG. In 1990, the entire Edgewood Area was put on the National Priority List and came under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA).

### **Purpose and Scope**

The purpose of this report is to (1) further define the hydrogeologic framework of the O-Field area, (2) characterize the hydraulic properties of the aquifers and confining units, and (3) define ground-water flow paths at O-Field on the basis of new data and new simulations of ground-water flow. This report presents the results of a study of the shallow ground-water-flow system at the Old and New O-Field sites at APG. The study refines an existing model of the shallow flow system and provides information on ground-water flow in the water-table aquifer with an emphasis toward New O-Field.

### **Description of Study Area**

The O-Field area is located on Gunpowder Neck of the Edgewood Area of APG, Harford County, Maryland (fig. 1). The study area is bounded on the north and east by Watson Creek and on the west by the Gunpowder River. H-Field is further to the south.

The Gunpowder River and Watson Creek are subject to some tidal flux. The stage of the Gunpowder River varies between 1 and 3 ft over the diurnal cycle, while the stage in Watson Creek varies depending on wind direction. Banks and others (1996) indicate that tidal cycles are often missed in Watson Creek (possibly due to adverse wind conditions). During these events, water continues to discharge from Watson Creek to the Gunpowder River through a culvert under Watson Creek Road.

The O-Field area is within the Coastal Plain Physiographic Province and is characterized by flat topography with low rolling hills. The land surface rises from near sea level at the Gunpowder

River and Watson Creek to about 15 ft above sea level at both Old O-Field and New O-field. An intermittent stream follows a channel between Old and New O-Fields and drains into Watson Creek. South of New O-Field, the land surface rises to between 20 and 25 ft.

The study area is underlain by unconsolidated deposits of Pleistocene and Cretaceous age that overlie Paleozoic and Precambrian crystalline bedrock. The shallow aquifers that are the subject of this report consist of Pleistocene and Holocene sediments. The Pleistocene sediments are primarily interbedded sand, silt, and clay of fluvial, estuarine and marginal marine origin (Owens, 1969). During sea-level regressive sequences, river channels were cut into the underlying Cretaceous sediments. The channels were filled with estuarine sediments during Pleistocene interglacial periods when sea level rose. These buried channels, called paleochannels, are common features of the Chesapeake Bay area. A paleochannel, probably formed as described above, was identified by Hughes (1993) 2 mi south of O-Field at J-Field.

### **Methods of Study**

Data from new borings and wells were used to modify the already existing hydrogeologic framework from Old O-Field (Vroblesky and others, 1989) to the New O-Field area. Data collected during the current study and by Vroblesky and others (1989) were evaluated for use in the ground-water-flow model, and a cross section of the hydrogeologic framework was constructed. Maps of the tops and thicknesses of the aquifers and confining units were compiled for New O-Field. Hydraulic properties of the aquifers and confining units were compiled on the basis of data from aquifer tests, slug tests, and chlorofluorocarbon age dating. Hydraulic head maps of the water-table and the upper confined aquifers were compiled on the basis of water levels measured in June 1993. Recharge to the water-table aquifer was evaluated using data from previous reports and interpretations of new data. Previous conceptual models of ground-water flow at O-Field were revised on the basis of those interpretations.

A previous USGS ground-water-flow model of the O-Field area, including the central and southern parts of Gunpowder Neck (Vroblesky and others, 1989), was modified to incorporate the new data. The Old and New O-Field areas within the current model were finely discretized to reflect the emphasis of the current study. The results of simulations made by use of a ground-water-flow model of the O-Field area developed for the U.S. Army by ICF Kaiser Engineers (1994) also were evaluated with regard to the hydrologic parameters it used. The current steady-state model was *calibrated using hydraulic heads measured in June 1993* and was used to determine ground-water flow paths.

### Previous Studies

The history of operations and early clean-up activities at O-Field was compiled from interviews and base records by Yon and others (1978). Nemeth and others (1983) reported chlorinated organic solvents and arsenic in ground water at O-Field and arsenic in Watson Creek and its bottom sediments. The U.S. Army Environmental Hygiene Agency reported organic and inorganic contaminants, including metals, in Watson Creek.

Vroblesky and others (1989) defined the hydrogeologic framework of the shallow aquifers at O-Field, characterized aquifer and confining-unit properties, determined the extent of contamination at O-Field and in Watson Creek, simulated ground-water flow of the O-Field area, and evaluated potential effects of various mitigation strategies on ground-water flow at O-Field. Hydraulic conductivity of the water-table aquifer was determined from constant rate and step-drawdown tests at Old O-Field (U.S. Army Corps of Engineers, 1994). In an interim Remedial Investigation Report for the U.S. Army, ICF Kaiser Engineers (1994) determined aquifer properties by aquifer tests, conducted several geophysical surveys (some in concert with the USGS), constructed geologic sections at New O-Field, and constructed a model to simulate ground-water flow. ICF Kaiser Engineers (1994) also further defined the extent, probable fate, and transport of contamination at New O-Field and in Watson Creek,

and conducted a benthic survey, a bioassay, and a baseline risk assessment. In 1992, the USGS collected passive soil-gas data at New O-Field. Discharge of ground water from the shoreline of Gunpowder Neck was investigated using thermal images flown by the National Oceanic and Atmospheric Administration (NOAA) on March 8 and 9, 1992 (Banks and others, 1996).

### Acknowledgments

The authors wish to thank the people and agencies whose help made this study possible. Ms. Cynthia Powels, Project Officer at DSHE, provided logistical support for the study. Joseph Beman of the USGS contoured the hydrogeologic maps in this report and made outstanding contributions to the field operations. Some of the hydrologic data used in this report were collected with the assistance of ICF Kaiser Engineers, who were under contract to the U.S. Army.

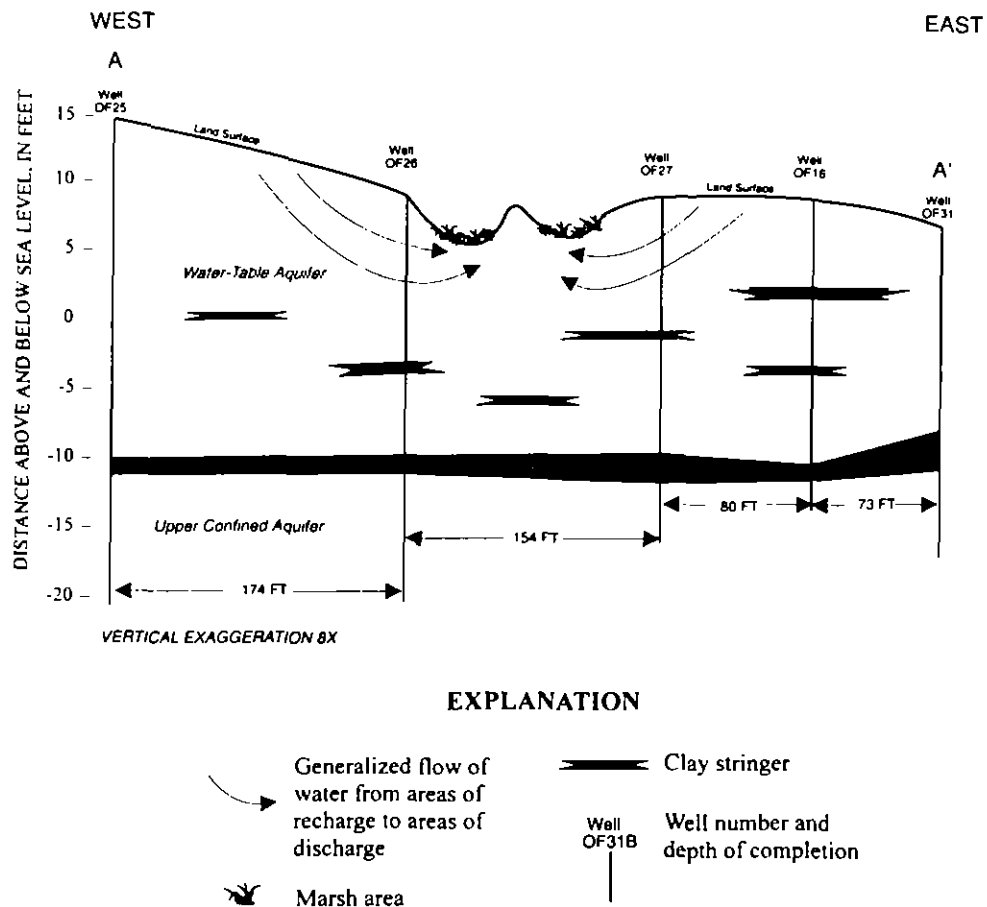
### HYDROGEOLOGIC SETTING

Data from previous studies (Vroblesky and others, 1989) indicate that three aquifers are present at O-field within a depth of about 120 ft. Investigation of the deepest of these aquifers, previously designated as the "lower confined aquifer" is beyond the scope of this report. This report focuses on data from new borings and wells drilled by ICF Kaiser Engineers and the U.S Army Corps of Engineers between 1991 and 1993. Chlorofluorocarbon data collected by the USGS at six wells were used to refine horizontal hydraulic conductivity values. Aquifer tests performed by ICF Kaiser Engineers were used to develop and refine an understanding of the hydrogeology. Precipitation data, collected between 1990 and 1993 from H-Field at APG, were used to determine a recharge rate to the water-table aquifer.

### Hydrogeologic Units

The hydrogeologic framework at O-Field was described previously by Vroblesky and others (1989). From land surface downward, the units include the "water-table aquifer", the "upper confining unit", and the "upper confined aquifer"





**Figure 3.** Hydrogeologic units and generalized direction of ground-water flow at New O-Field.

(fig. 3). These units are either within the Pleistocene Talbot Formation or more recently reworked alluvium of the Holocene. The geology of Harford County, which includes the O-Field area, was described in a report by Owens (1969).

#### **Water-Table Aquifer**

The water-table aquifer consists of a sequence of saturated sediment, which is mostly quartz sand interbedded with silt and clay, that extends throughout Gunpowder Neck. This sequence ranges in thickness at the O-Field area from 13 to 23 ft. These sediments were deposited in rivers, wetlands, and streams during the Pleistocene Epoch. During the Holocene, some of the sediments have been eroded and redeposited along the banks of and beneath the present tidal rivers, wetlands, and estuaries.

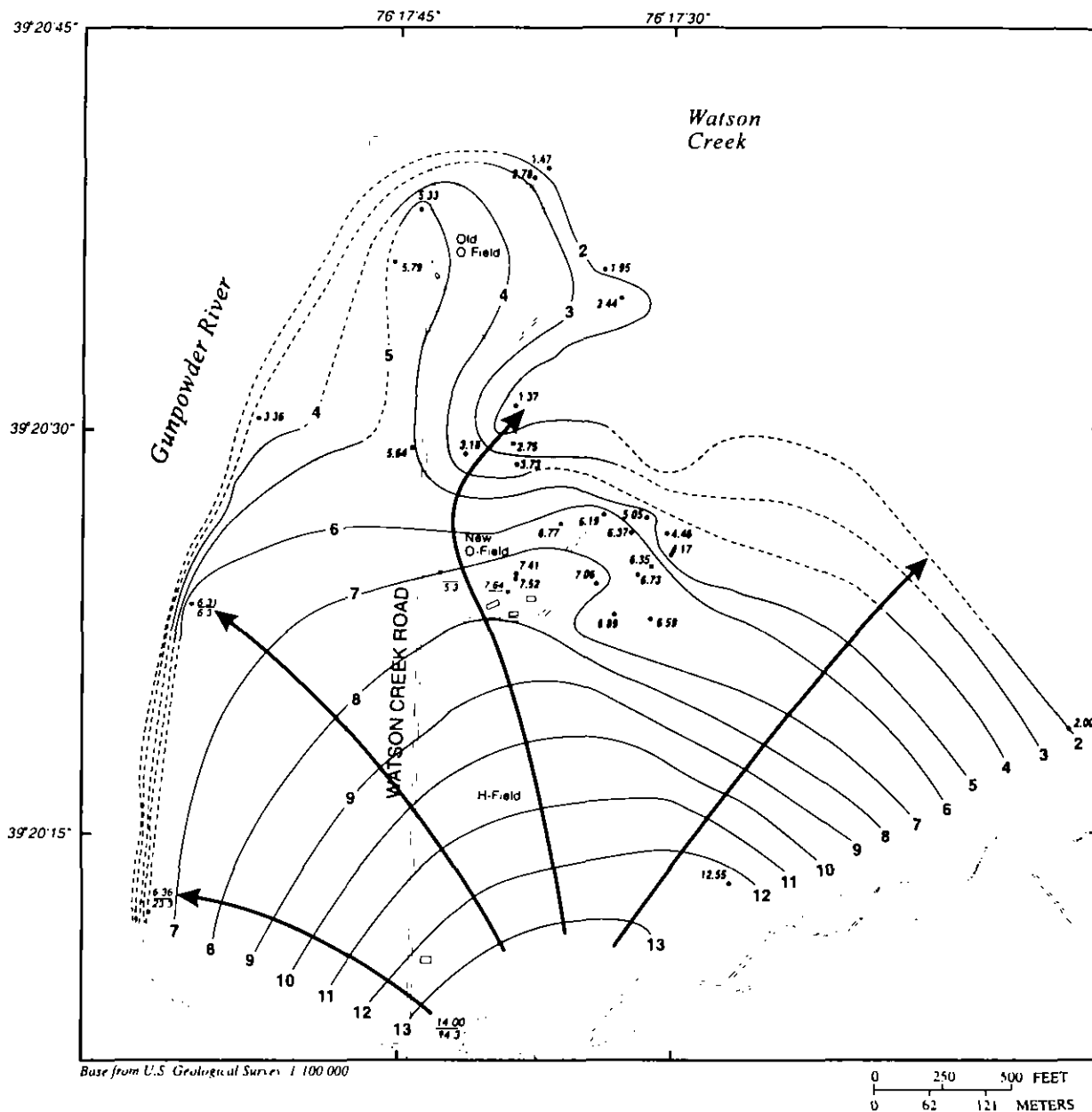
The sand of the water-table aquifer ranges in size from fine grained to coarse. Gravel is mixed

with the sand in some places as indicated by a few lithologic logs from boreholes. Sieve analyses of several samples of the aquifer indicated an average of 80 percent sand, 19 percent silt, and 0.09 percent gravel (ICF Kaiser Engineers, 1994).

The water table is the upper surface of the saturated zone where the hydraulic pressure is equal to atmospheric pressure. It is, by definition, unconfined (fig. 4). Beneath Old O-Field and to a lesser degree beneath New O-Field, the bottom of the water-table aquifer is confined by a clay layer termed the "upper confining unit."

#### **Upper Confining Unit**

The upper confining unit is a sequence of fine-grained sediments beneath the water-table aquifer. It is composed primarily of silt and clay mixed with fine sand. Three samples from the upper confining unit at New O-Field averaged 58 percent silt or clay, 41 percent sand, and 0.6 percent gravel



#### EXPLANATION

• 2.44 LOCATION OF WELL.  
Used to determine altitude  
of the potentiometric  
surface. Number is  
altitude, in feet above  
sea level.

• 14.00  
14.3 WELLS SAMPLED FOR  
CHLOROFLUOROCARBON  
AGE DATA-Top number is  
altitude of water level,  
in feet above sea level.  
Bottom number  
is years since recharge.  
Dashes indicate data  
unavailable.

2 POTENTIOMETRIC SURFACE  
CONTOURS- Dashed  
where approximately  
located. Contour interval  
is 1 foot. Datum is sea level.

↗ FLOW LINES- Arrows  
indicate general  
direction of ground-  
water flow.

Figure 4. Altitude of the water table and flow lines at O-Field, June 1993.

(ICF Kaiser Engineers, 1994). The sediments range in color from black to gray or greenish gray (Vroblesky and others, 1989).

The clay content of the upper confining unit is greater beneath Old O-Field than beneath New O-Field. In places, particularly at New O-Field where the upper confining unit contains a large proportion of sand, the upper confining unit is difficult to distinguish from the water-table aquifer.

The top of the upper confining unit is about 4 ft below sea level near Watson Creek Road and about 12 to 16 ft below sea level beneath Watson Creek (fig. 5). The top of the unit slopes to the east beneath Old and New O-Fields; however, the surface undulates, indicating that it has been partially eroded in places by streams or that the

thickness of the unit varied at the time of deposition.

According to Vroblesky and others (1989), undisturbed parts of the upper confining unit were probably thicker beneath Old O-Field than beneath New O-Field. Furthermore, trenches may have been dug through the upper confining unit in many places at both Old and New O-Fields. In addition, data from borings at New O-Field showed that the upper confining unit is considerably thinner beneath New O-Field. The upper confining unit ranges from approximately 1 to 4 ft thick at Old O-Field, but in most of New O-Field, it is approximately 1 ft thick or less (fig. 6). The water-table aquifer could, therefore, be hydraulically connected to or poorly separated from the upper confined aquifer in some places.

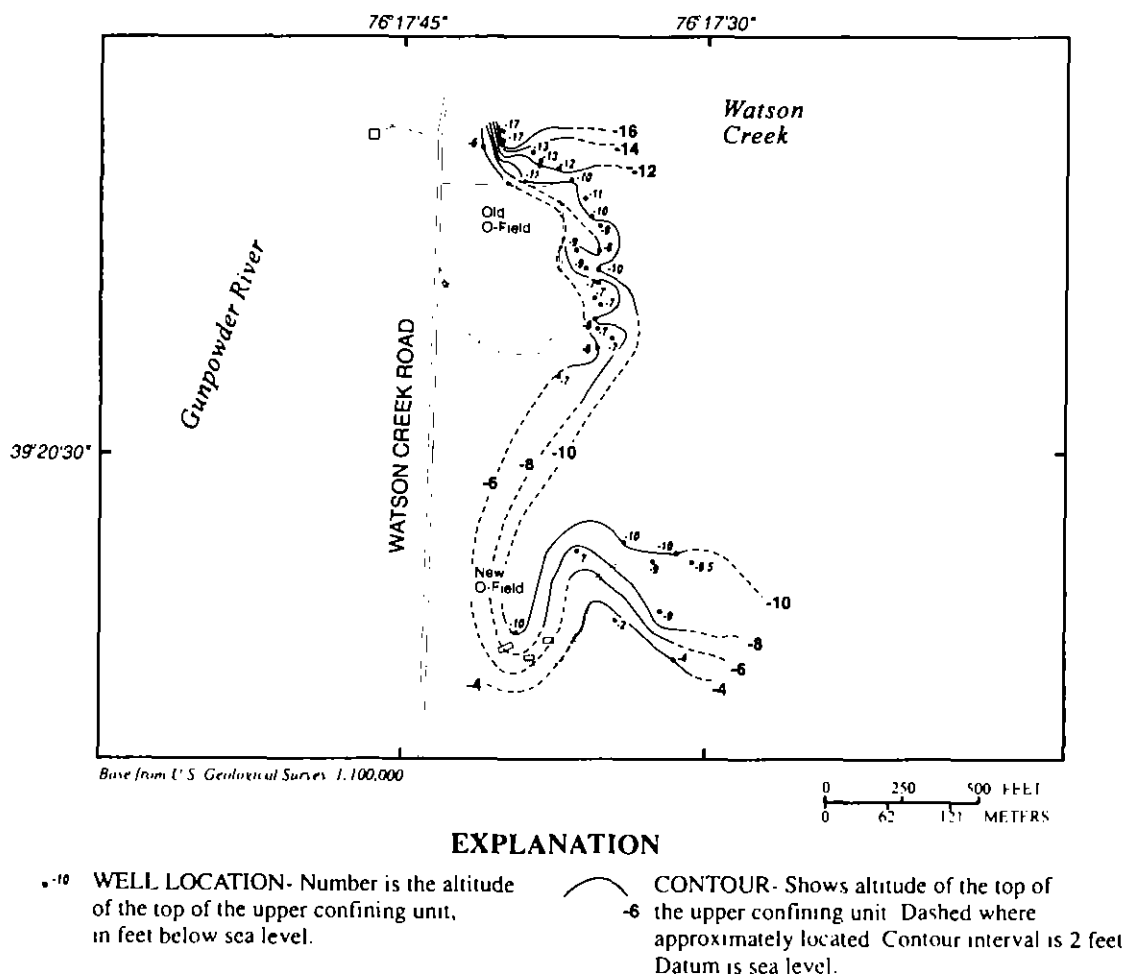
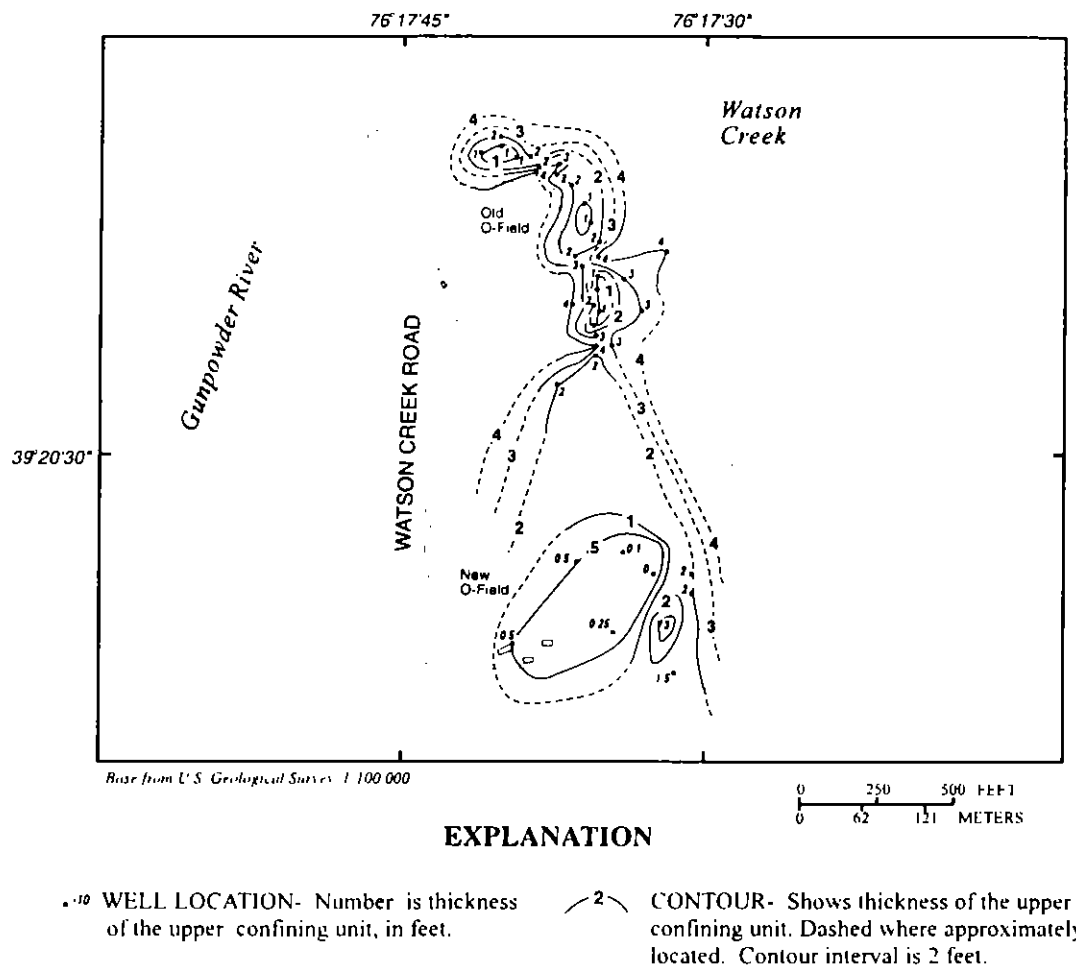


Figure 5. Altitude of the top of the upper confining unit at O-Field.



**Figure 6.** Thickness of the upper confining unit at O-Field.

### Upper Confined Aquifer

Beneath the upper confining unit is a sand and gravel aquifer interbedded with clay throughout most of the O-Field area. The sand is dark gray to brown and ranges in grain size from coarse to medium. Ten samples from the upper confined aquifer at Old and New O-Fields averaged 18 percent gravel, 63 percent sand, and 19 percent silt (ICF Kaiser Engineers, 1994). The gravel, sand, and silt were deposited by Pleistocene rivers and streams.

The upper confined aquifer is bounded by less permeable silt and clay layers above and by a thick clay layer below. Water in a confined aquifer is under pressure and the hydraulic heads of the aquifer at depth are typically higher than the elevation of the top of the confined aquifer.

The upper confined aquifer is continuous beneath the O-Field area, but thins to the west and may have been eroded and replaced by finer-grained sediments beneath the Gunpowder River. The upper confined aquifer ranges in thickness from 2 to about 13 ft.

### Lower Confining Unit

The lower confining unit is a dark gray to black clay that contains abundant leaf and plant fossils (Vroblesky and others, 1989). One sample from this unit collected at New O-Field was composed of 98 percent silt or clay and 2 percent sand (ICF, Kaiser Engineers, 1994).

The clay was probably deposited in a marginal marine or estuarine environment (Owens, 1969). The lower confining unit is a continuous and relatively thick unit, averaging about 50 ft thick beneath Old O-Field.

## Water-Level Changes and Recharge

Continuous recorders were used to monitor water levels in selected wells during this investigation. Analysis of well hydrographs indicates daily or seasonal recharge events and the effects of tides on the aquifers. Rates of recharge to the water-table aquifer were calculated using data from previous reports and interpretations of new data. These recharge rates were then tested in the current ground-water-flow model to determine which rate (or rates), when compared with combinations of hydraulic conductivity, transmissivity, and leakance, provided the most accurate representation of heads in the water-table and upper confined aquifers.

Precipitation at H-Field ranged from 35.55 to 46.08 in/yr from 1990 (when the station was established) to 1993 and averaged 41.08 in/yr, with a standard deviation of 3.98 in/yr (Wayne Kaiser, U.S. Army Test and Evaluation Command, oral commun., 1994). Rasmussen and Andreasen (1959) and Harsh and Lacznia (1990) indicated that ground-water recharge can range between 31 and 52 percent of total precipitation. Based on these percentages and the 41.08 in/yr average for precipitation at O-Field, recharge to the water-table aquifer is estimated to range between 12.7 and 21.4 in/yr. In order to consider a wide range of possible recharge values, values of one and two standard deviations above and below the mean precipitation (41.08 in/yr) were calculated, yielding five precipitation values. Each of these values was then multiplied by the high (52 percent) and the low (31 percent) recharge rate to yield 10 recharge values. The 10 values ranged from 10.26 to 25.5 in/yr and were used in the ground-water-flow model as described above.

A recharge value of about 9 in/yr was used in a previous flow model of the O-Field area by ICF Kaiser Engineers (1994). Vrobley and others (1989) indicated that recharge in the O-Field area ranged from 12.5 to 13 in/yr depending on the clay content of the soil zone and how the water-table aquifer responded to rainfall.

## Water-Table Aquifer

The water-table aquifer is recharged primarily by precipitation directly on Gunpowder Neck. A small amount of rainfall and snowmelt is carried in runoff to the Gunpowder River and to Watson Creek. A larger part of the precipitation is evaporated at land surface or is taken up by plants and transpired. The remaining precipitation infiltrates through the unsaturated zone to recharge the water table.

Water levels in wells screened in the water-table aquifer tend to rise in the winter and early spring, indicating a seasonal recharge when plants are dormant and recharge is relatively high (fig. 7). Water levels tend to decline in the late spring and throughout the growing season from summer to early autumn when there is low or negligible recharge. The water table thus fluctuates with the seasons, but the fluctuations and the mean are consistent from year to year.

### Upper Confining Unit

The upper confining unit inhibits water flowing between the water-table aquifer and the upper confined aquifer. The volume of water leaking through the upper confining unit is small and the flow rate is slow compared to movement through the water-table aquifer.

The upper confining unit varies in lithology and thickness and may not be continuous throughout the O-Field area. Recharge to the upper confined aquifer could be substantial where the upper confining unit is sandy and thin or breached by paleochannels or trenches.

### Upper Confined Aquifer

Water levels in the upper confined aquifer (fig. 3) are under pressure and respond to changes in pressures imposed on the water-table aquifer. Beneath the higher land surface altitudes, the confined aquifer responds to loads (depending on how well it is confined) imposed by major changes such as seasonal increases or decreases in the volume of water stored in the water-table aquifer. Daily rises and subsequent declines in water levels caused by major recharge events can also cause sharp increases and declines in the pressure heads.

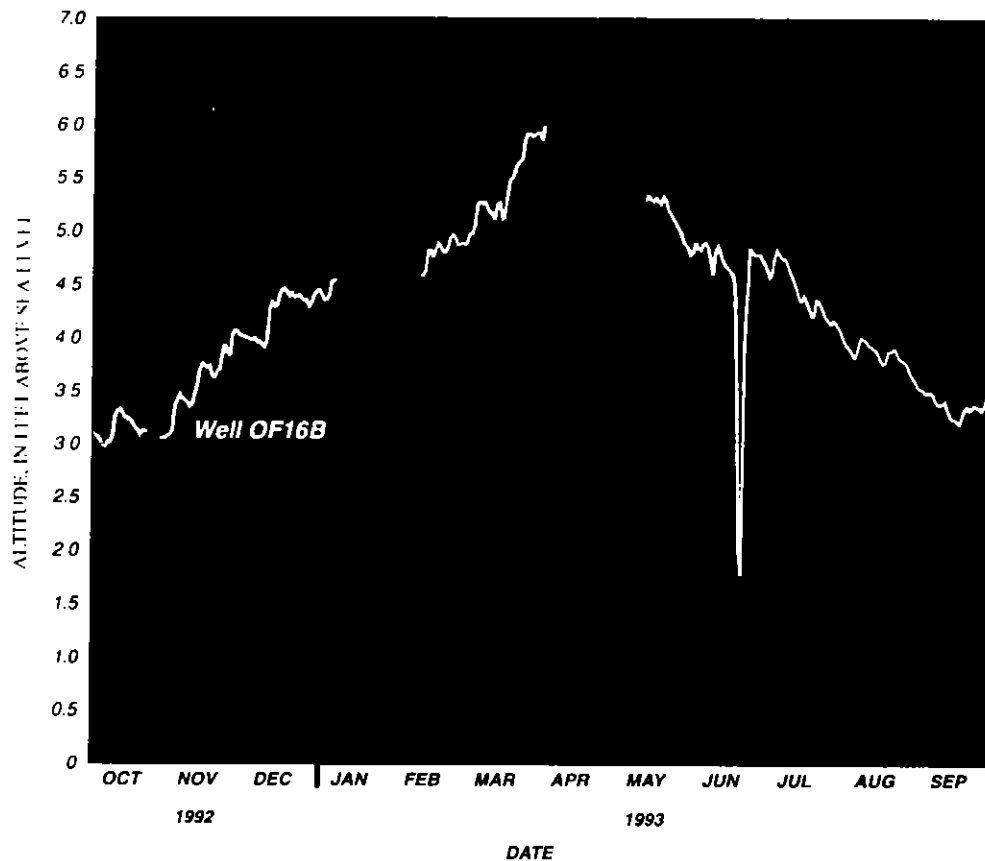


Figure 7. Altitude of the water table in well OF-16A and the potentiometric surface of the upper confined aquifer in well OF-16B at New O-Field, October 1, 1992 through September 30, 1993.

Near the shore and the tidal wetlands, the water levels of the upper confined aquifer respond to changes in tidal loads. Tides in Watson Creek, however, are heavily influenced by winds and frequently do not show a diurnal response. In the absence of a tidal stress in Watson Creek, heads in the upper confined aquifer do not show a response.

The upper confined aquifer is covered by silt and clay layers above and is bounded by a clay layer below. Although confined, the aquifer is recharged by water leaking through the upper confining unit from the water table. Because the vertical hydraulic conductivity of the upper confining unit is likely to be much lower than that of the water-table aquifer, the recharge rate through the upper confining unit is probably much smaller than the recharge rate to the water-table aquifer. Where the upper confining unit is missing or more

permeable (more sand and less silt or clay), recharge rates could approach those of the water-table aquifer.

## HYDRAULIC PROPERTIES

The hydraulic conductivities of aquifers and confining units control, to a large degree, the movement of ground water and the speed and directions that contaminants in ground water can travel. The vertical hydraulic conductivity of the upper confining unit and its thickness are significant factors governing the flow of ground water and contaminants between the water-table aquifer and the upper confined aquifer, and Watson Creek or the Gunpowder River. Hydraulic conductivities of the units at O-Field have been investigated by various methods in previous studies, and are summarized below.

### **Water-Table Aquifer**

Step-drawdown tests done at Old O-Field by the U.S. Army Corps of Engineers (1994) and aquifer tests at New O-Field by ICF Kaiser Engineers (1994) showed an average horizontal hydraulic conductivity of about 30 ft/d for the water-table aquifer. A value of 20 ft/d for horizontal hydraulic conductivity was used in a ground-water-flow model done by ICF Kaiser Engineers. A ground-water-flow model of Gunpowder Neck developed by the USGS (Vroblesky and others, 1989) used a range in values of 5 to 110 ft/d in the O-Field area. Results of slug tests at Old O-Field by Vroblesky and others (1989) indicated an even greater range in the hydraulic conductivity of the water-table aquifer of less than 0.1 ft/d to about 200 ft/d. The values less than 0.1 ft/d are considered to have resulted from the presence of fine particles, which were not removed during well construction, and did not represent aquifer material (Vroblesky and others, 1989).

### **Upper Confining Unit**

The vertical hydraulic conductivity of the upper confining unit and its thickness are significant factors governing the flow of ground water and contaminants between the water-table aquifer and the upper confined aquifer and Watson Creek or the Gunpowder River. Vertical hydraulic conductivity ranged from 0.0002 to 0.001 ft/d for the upper confining unit in the flow model developed by Vroblesky and others (1989). ICF Kaiser Engineers (1994) calculated a vertical hydraulic conductivity of 0.02 ft/d at New O-Field on the basis of simulations of the aquifer tests and estimated 0.01 ft/d for Old O-Field.

### **Upper Confined Aquifer**

The horizontal hydraulic conductivity of the upper confined aquifer ranges from 20 to 30 ft/d and averages 22 ft/d on the basis of drawdown and recovery tests at two New O-Field sites (ICF Kaiser, Engineers, 1994). A hydraulic conductivity value of 20 ft/d was used by ICF Kaiser Engineers (1994) for the upper confined aquifer in a flow model of the O-Field area. On the basis of slug tests analyzed by the Hvorslev method (Hvorslev, 1951) for six wells that were purged of

fine material near the well screen, hydraulic conductivity of the upper confined aquifer ranges from 18 to 63 ft/d with a median of 31 ft/d (Vroblesky and others, 1989). In their flow model, Vroblesky and others (1989) used a range of transmissivities for different areas representing the lower confined aquifer.

### **Lower Confining Unit**

Laboratory analyses of six cores from two sites at Old O-Field showed that the vertical hydraulic conductivity ranged from  $4.7 \times 10^{-6}$  to  $4.7 \times 10^{-4}$  ft/d with a median of  $1.6 \times 10^{-5}$  ft/d (Vroblesky and others, 1989). The low hydraulic conductivity and thickness of this unit make it a relatively impermeable lower boundary for the aquifers of interest in this report.

## **GROUND-WATER FLOW**

Water levels were monitored in 31 wells in the water-table aquifer and in 21 wells in the upper confined aquifer from October 1992 through September 1993. The shallow aquifer system of the O-Field area is comprised of the water-table aquifer, the upper confining unit, and the upper confined aquifer (fig. 3). Because ground-water movement through the lower confining unit is negligible, it is considered a lower boundary to the shallow aquifer system.

### **Ground-Water-Flow Directions and Discharge Areas**

Water levels in the water-table aquifer tend to be highest in late winter and early spring, decline throughout the summer, and reach yearly lows in September or October. Average head values for the year would therefore be found during mid-summer or mid-winter. For the current ground-water-flow model, heads measured in June 1993 were chosen to represent steady-state conditions. Water-level maps of the aquifer were drawn from hydraulic heads measured in June 1993. Directions of ground-water flow and discharge areas are derived from interpretation of these maps.

### **Water-Table Aquifer**

The water table is located a few feet beneath land surface and roughly follows topographic contours. The water table slopes from higher altitudes

at the southern and central part of the study area northward and outward toward the wetlands between Old O-Field and New O-Field, Watson Creek, and the Gunpowder River (fig. 4).

The ground-water flow is horizontal, in linear or slightly curved paths perpendicular to the equipotential lines. The direction of ground-water flow is from the higher hydraulic heads beneath the land to the lower heads beneath the wetlands and tidal rivers near the shore. Ground water moves from the water-table aquifer to the shore, where it discharges. A small amount of ground water also leaks downward through the upper confining unit and provides recharge to the upper confined aquifer.

#### Upper Confining Unit

Because of the large differences in hydraulic conductivities between the aquifers and the confining unit, the direction of movement through the fine-grained sediments is predominantly vertical. In recharge areas beneath the higher land surfaces, ground water moves downward through the confining unit. In discharge areas near and beneath the tidal rivers and wetlands, ground water moves upward through the confining unit. For example, water from the upper confined aquifer discharges by upward leakage through the bottom sediments of Watson Creek.

#### Upper Confined Aquifer

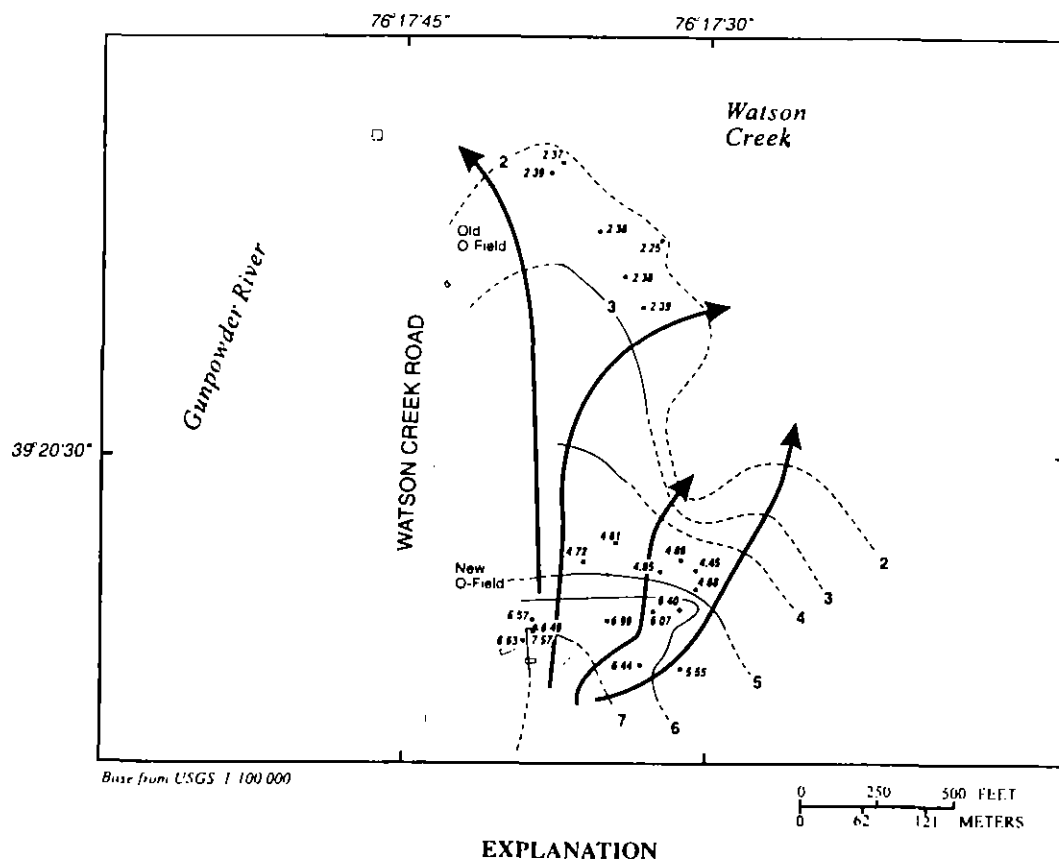
The potentiometric surface of the upper confined aquifer is similar to that of the water-table aquifer in that the highest heads are to the south and beneath the center of the study area. Ground water flows in linear or curved paths from the higher potentiometric heads beneath the southern and central parts of the study area toward the lower heads beneath the shore of the Gunpowder River and Watson Creek. The hydraulic heads and gradients are lower in the upper confined aquifer than in the water-table aquifer (fig. 8). Beneath the tidal creeks and wetlands, heads in the upper confined aquifer are probably higher than sea level and ground water from the upper confined aquifer discharges by upward leakage through confining units and other sediments beneath these surface-water bodies.

#### Chlorofluorocarbon Dates

The age of water samples collected from the wells was determined by use of chlorofluorocarbon methods and then used to estimate ground-water-flow rates (Busenberg and Plummer, 1992). Chlorofluorocarbons (CFC's) are synthetic, chemically stable compounds that have been manufactured since the 1930's for use as refrigerants and solvents, propellants in aerosols, and foaming agents in plastics. CFC's are persistent in the environment (virtually all that are manufactured eventually are released into the atmosphere), and are resistant to microbial degradation in aerobic ground-water systems (Thompson and Hayes, 1979). Two CFC's in particular, CFC-12 ( $\text{CCl}_2\text{F}_2$ ) and CFC-11 ( $\text{CCl}_3\text{F}$ ), make up over 77 percent of the  $10^9$  kilograms produced annually in the global market, with worldwide annual production currently increasing at a rate of approximately 3.7 percent (Busenberg and Plummer, 1992). The atmospheric concentrations of these compounds from 1940 to 1977 have been estimated from production records. From 1977 to the present, concentrations have been determined from semiannual averages of measured atmospheric concentration (Busenberg, and others, 1993).

By the mid-1970's, it was recognized that detectable CFC concentrations in natural water held potential as an environmental tracer for water recharged after 1945. Thompson (1976) and Thompson and Hayes (1979) conducted studies in New Jersey, Texas, and Arkansas that showed that CFC-modeled age dates agree with dates based on known hydrologic parameters and tritium ( $^3\text{H}$ ) concentrations. The qualitative implication of CFC's in ground water is that some or all of the sampled water contains post-1945 water. Because CFC concentrations in the atmosphere are continuously increasing, concentrations of CFC's in ground water will continuously increase as new precipitation recharges the aquifer. In order to estimate water age from CFC concentrations, it is assumed that the recharged water maintains equilibrium with the air in the unsaturated zone prior to incorporation into the water table. For





- 472 WELL- Used to determine altitude of the potentiometric surface. Number is altitude, in feet above sea level.
- 2 POTENTIOMETRIC SURFACE CONTOURS- Dashed where approximately located. Contour interval is 1 foot. Datum is sea level.
- FLOW LINES- Arrows indicate general direction of ground-water flow

Figure 8. Potentiometric surface of the upper confined aquifer and flow lines at O-Field, June 1993.

hydrologic settings similar to the O-Field study area where depth to ground water is shallow (less than 20 ft), it is assumed that CFC concentrations in the unsaturated zone do not differ significantly from those in the atmosphere (Weeks and others, 1982).

#### Factors Influencing Concentrations

Henry's law is used to calculate the partitioning of CFC-12 and CFC-11 between the atmosphere in the unsaturated zone and the ground water. The Henry's law constants for CFC-12 and CFC-11 were calculated from their solubilities under environmental conditions. Recharge temperatures of O-Field ground water were based on the dissolved concentrations of argon and nitrogen incorporated at equilibrium with the atmosphere at the time of recharge (Heaton, 1981; Heaton and Vogel, 1981). The methods used to sample and analyze dissolved gases are described in Pearson and others (1978) and by Busenberg and others

(1993). The method involves bringing a water sample in a closed container of known volume into contact with an evacuated container of known volume. After equilibration, the head space in the sample container is analyzed for  $N_2$ ,  $O_2$ ,  $CO_2$ , Ar, and  $CH_4$  by use of a gas chromatograph. The concentration of the dissolved gases in the aquifer is determined by summing the amounts present in the two phases and dividing by the volume of the water chamber. Using this method, dissolved gas concentrations measured in the O-Field area indicate a recharge temperature of approximately  $12 \pm 2^\circ C$ .

CFC concentrations in ground water may be influenced by microbial degradation, soil sorption, modern air in the sample, hydrologic processes such as hydrodynamic dispersion and mixing at the well screen, and contamination. Of these phenomena, contamination from atmospheric and non-

atmospheric sources represents the largest potential source for error at the O-Field site. Contaminated CFC samples are defined as samples with concentrations that exceed the range possible for air/water equilibrium at the determined recharge temperature. For water recharged at 12°C in equilibrium with 1993 atmosphere, concentrations of CFC-12 would be expected to be about 328.4 picograms per kilogram (pg/kg) and CFC-11 would be about 723.5 pg/kg. Because of the potential for CFC contamination at the O-Field site and because errors associated with CFC sampling are orders of magnitude greater than those associated with CFC analysis, the ages shown in table 1 are the older of either the CFC-12 and CFC-11 ages. In samples that have been contaminated through nonatmospheric sources, actual water ages will be older than reported on the basis of CFC age modeling.

Samples taken from wells OF-23 and OF-37 were contaminated with CFC's (table 1). Well OF-23 had 128,752 pg/kg of CFC-12 and an unquantifiable amount of CFC-11; well OF-37 had 5,108 pg/kg of CFC-12 and 12,582 pg/kg of CFC-11. Well OF-23 had 393 times the amount of CFC-12 while well OF-37 had 16 and 17 times the expected amounts for CFC-12 and CFC-11 for 1993 atmosphere, respectively (table 1). In previous studies, CFC contamination has been attributed to PVC well casing, and/or Teflon<sup>1</sup> or rubber pump parts (Dunkle and others, 1993). Given the disposal history of the area, however, it is more probable that CFC contamination at O-Field was a direct result of disposal or decontamination actions performed in the area. Although Nemeth (1989) does not specifically describe activities that would directly contribute to CFC contamination at O-Field, he does identify activities on post, process cooling and degreasing, in particular, that probably used CFC's.

<sup>1</sup>The use of brand, firm, or trade names in this report is for identification purposes only, and does not constitute endorsement by the U.S. Geological Survey.

**Table 1.** *Chlorofluorocarbon data for wells at New O-Field, Aberdeen Proving Ground, Maryland (Samples taken from wells OF-23 and OF-37 were contaminated with chlorofluorocarbons)*

[pg/kg, picograms per kilogram; nd, no data available; --, age data not available due to sample contamination]

Well no.	Date collected	Time collected	Recharge temperature (F)	CFC-11 (pg/kg)	CFC-12 (pg/kg)	Age (years) <sup>a</sup>
OF-3	10/26/93	1000	12	437	275	14.3
OF-9	10/27/93	1700	12	166	199	23.3
OF-10	10/27/93	1100	12	652	268	<sup>b</sup> 6.3
OF-23	10/25/93	1200	12	nd	128,752	--
OF-37	10/28/93	1000	12	12,582	5,108	--
OF-39	10/28/93	1400	12	674	349	5.3

<sup>a</sup> Ages based on CFC-11 data unless otherwise noted

<sup>b</sup> Based on CFC-12 data

Physical processes (such as mixing of ground water in the well annulus) can also introduce uncertainties into the interpretation of CFC data. Mixing of ground water can occur if a well is located in an area of ground-water discharge where flow lines of different ages converge. Mixing also can occur if a well is screened across multiple aquifers, drawing multiple age waters into the well bore. Once ground-water sources are mixed, CFC data cannot be used to distinguish water from different recharge years.

#### Sampling and Analysis

Busenberg and Plummer (1992) and Dunkle and others (1993) describe CFC sampling procedures, laboratory methods, and analysis. The wells at the O-Field site were sampled on October 25-28, 1993, by use of a submersible reciprocating-piston Bennett pump constructed of stainless steel with 0.25-in. copper discharge line. Pumping rates during purging and sampling typically ranged from approximately 0.5 to 1.0 gal/min, depending on well yield. Four to six

samples at each well were collected in 63-milliliter (mL) borosilicate glass ampules and preserved in the field by sealing the ampule without allowing the sample to contact the atmosphere. The apparatus for collecting the samples is described in Busenberg and Plummer (1992). Sample analysis involved the use of a purge-and-trap gas chromatograph with an electron capture detector (ECD). Independent model ages were derived for CFC-11 and CFC-12 for each of the ampules collected at each site by comparing sample concentrations to the atmospheric growth curve (Busenberg and others, 1993). An independent model age was derived for CFC-11 and CFC-12 from each of the sample vials associated with a given sample. For the current study, the smallest concentration of CFC-11 or CFC-12 for each ampule was used to determine CFC modeled age. Errors in CFC concentrations introduced from field procedures tend to be larger than errors introduced during laboratory analysis. In environments where sampling conditions are less likely to be the major contributor to sample error, however, variance for CFC modeled ages range from 24 to 36 months (Eurybiades Busenberg, U.S. Geological Survey, oral commun., 1995).

Well-selection criteria were based on the location of the site upgradient of or sufficiently distant from known disposal areas. This was particularly important because chlorinated organic solvents were disposed of at many sites around the O-Field area (Nemeth, 1989). These solvents can potentially mask CFC signatures during analyses.

Six wells (OF-3, 9, 10, 23, 37, and 39) near Old and New O-Fields were sampled for CFC's to better refine estimates of the rate of ground-water movement (fig. 4). All wells, except OF-39, were screened in the water-table aquifer. All wells, including OF-39, were thought to be approximately located along areal flow-path lines (fig. 4). All wells are constructed of polyvinyl chloride (PVC). All wells, except OF-39, were drilled using hollow-stem auguring techniques and screened in the water-table aquifer using 10 ft of 0.01-in. screen. Wells OF-9 and OF-10 are 2 in. in diameter and wells OF-3, OF-23, and OF-37 are 4 in. in diameter. Well OF-39 was constructed by use of mud rotary drilling techniques. Well OF-39

is 6 in. in diameter and has a 25-ft long, 0.01-in. screen that penetrates both the water-table and upper confined aquifers.

#### Application to Ground-Water Flow

CFC age dates can provide an empirical method of refining the simulated physical properties of the aquifer used to calibrate a ground-water-flow model. This is done by comparing rates of water movement calculated from the CFC data to average velocities calculated using the following equation for average rate of movement of water through a porous media (Lohman, 1979):

$$v = (K/\theta) (dh/dl), \quad (1)$$

where:

$v$  = average velocity (ft/d),  
 $K$  = horizontal hydraulic conductivity (ft/d),  
 $dh$  = change in head (ft),  
 $dl$  = distance between the wells (ft), and  
 $\theta$  = effective porosity (unitless).

Average ground-water velocity under a given set of hydraulic conditions was determined in three ways: (1) head data measured in the field were used in the velocity equation above and assumed values for effective porosity and horizontal hydraulic conductivity were used; (2) the velocity equation was used with model-derived heads and the same assumed values for effective porosity and horizontal hydraulic conductivity as in (1) above; and (3) the distance between two wells along a flow path was divided by the difference in CFC-derived ages to attain an average velocity based exclusively on CFC data. The flow model could be calibrated to the CFC data by iteratively changing one of the assumed hydraulic parameters and comparing the resulting velocity values to those calculated from the CFC modeled age data.

The value used for  $dl$  remained a constant 1,274 ft for all simulations. The values for  $dh$  reflected either measured or modeled heads. Effective porosity values ranging from 0.25 to 0.45 were considered on the basis of the description of

others (1989) as composed of medium-grained sand with interbedded silt and clay. Johnson (1967) indicated these sediments can have porosities ranging from about 0.38 to 0.48. Porosities were varied in 0.05 increments. For all velocity calculations, using both measured and modeled heads, an effective porosity value of 0.4 was found to provide the closest match with CFC age data. A horizontal hydraulic conductivity value of 28 ft/d for the water-table aquifer was found to provide reasonable values for velocity. This value was determined by the calibrated flow model described in the following section.

### **Ground-Water-Flow Simulation**

A previous USGS ground-water-flow model of the O-Field area (Vroblesky and others, 1989) was redesigned using new aquifer-test data and was rediscritized in the vicinity of New O-Field. The current model expanded the modeled domain from Vroblesky and others (1989) so that model boundaries extended well beyond the area of interest. The current model was calibrated to water levels of June 1993. The current model was designed to determine aquifer properties and directions of ground-water flow.

### **Model Grid and Boundary Conditions**

The USGS modular finite-difference ground-water-flow model (McDonald and Harbaugh, 1988) was used for the previous and the current model of the O-Field area. The current O-Field model extended the grid so that the grid boundaries would not influence model results. The current model also increases the discretized area to cover both Old and New O-Field. Like the original model, the current model simulates flow in the water-table aquifer, the upper confining unit, and the upper confined aquifer for part of Gunpowder Neck. Vertical leakage from the lower confining unit beneath the upper confined aquifer was assumed to be negligible.

As in the previous model, a two-layer aquifer system was simulated with vertical leakance calculated between the layers (fig. 9). The water-table aquifer was simulated as one distinct layer in the current model and designated as "unconfined." The upper confined aquifer was simulated as the

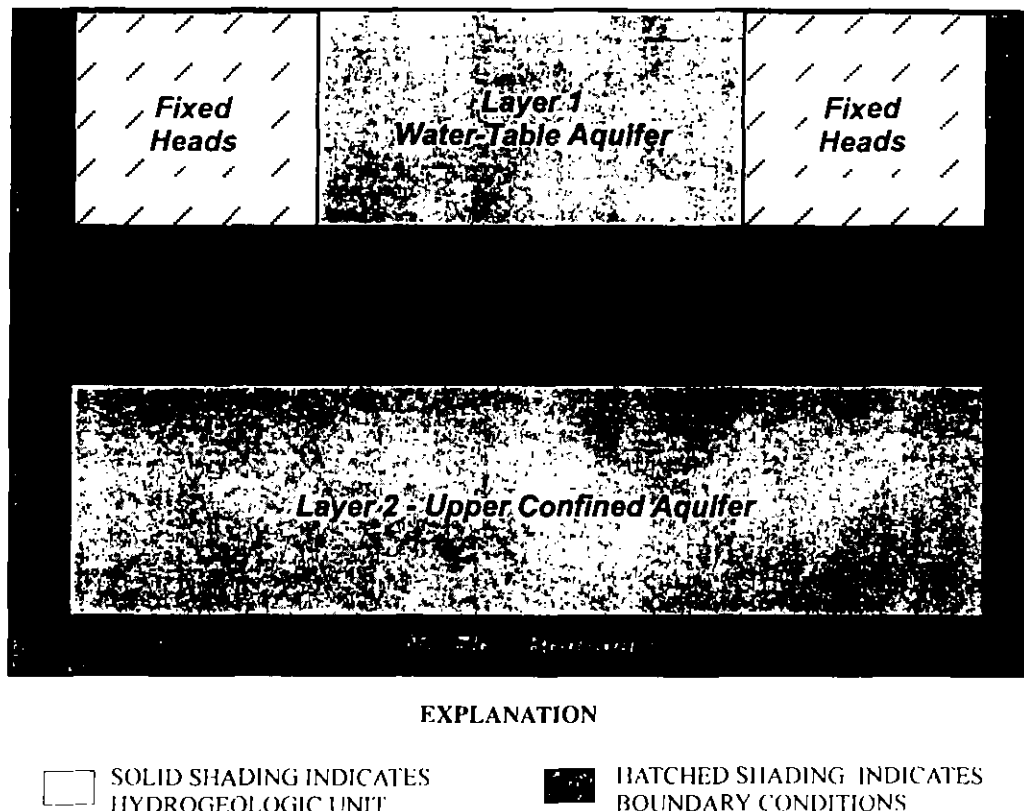
second layer and designated as "confined" during all simulations. Vertical leakage between the water-table aquifer and the upper confined aquifer was simulated for each cell by a hydraulic conductance term that includes values for vertical hydraulic conductivity and thickness of the confining unit. In this configuration, hydraulic heads are calculated by the model for the water-table and the upper confined aquifer, but not for the upper confining unit between the two aquifers. See McDonald and Harbaugh (1988, p. 2-35) for a general description of the method.

A variable-sized grid (fig. 10) containing 88 rows and 105 columns was constructed and merged to various map coverages of Gunpowder Neck, Watson Creek, and the Gunpowder River by use of a geographic information system (GIS). The smallest cell sizes (block centered nodes) were used to simulate ground-water flow at the Old and New O-Field sites and are 25 ft on a side. The grid and cell size expand outward from the Old and New O-Field area where less definition of ground-water flow is required.

Lateral boundaries of the model (fig. 10) were placed far from the areas of interest so that they would not artificially affect the simulated results. A constant head value of 0.9 ft was used in cells representing the Chesapeake Bay and Gunpowder River. Tidal data were collected from a tide gage located on the culvert at the mouth of Watson Creek. The median tidal value for 1993 (January through December) was 1.15 ft above mean sea level. This value was used to represent the constant head in Watson Creek as well as the adjoining wetlands. As in the model created by Vroblesky and others (1989), a line of drains representing the wetland between the Old and New O-Field sites was included in the top layer, the water-table aquifer.

### **Calibration**

The model was calibrated to water levels measured in June 1993 in 31 wells screened in the water-table aquifer and 21 wells screened in the upper confined aquifer. For each computer run of the calibration phase, the measured water level at each well was compared to the simulated water



**Figure 9.** Major hydrogeologic units and boundary conditions modeled at New O-Field.

level at that well and the differences were squared and then summed. A large sum of squared errors for a run indicated a poor simulation of measured water levels. A low sum of errors indicated a better approximation. By incrementally changing model variables and plotting the sum of squared errors for each model run on a two-dimensional matrix, a visual representation of model accuracy can be displayed (fig. 11).

A horizontal hydraulic conductivity of 28 ft/d was initially assigned for the entire water-table aquifer based on a median value from aquifer tests performed by ICF Kaiser Engineers (1994), the U.S. Army Corps of Engineers (1994), and Vroblesky and others (1989). This value was later refined to include an area of lower horizontal hydraulic conductivity (5.0 ft/d) around the New O-Field site (fig. 12). This assumption of lower hydraulic conductivity near Watson Creek is

supported by Banks and others (1996) in their analysis of thermal imagery of the area. Thermal image data collected on March 8 and 9, 1992, showed that areas of Watson Creek northwest of New O-Field had a cooler thermal signature than did the main body of Watson Creek. This was attributed to decreased ground-water discharge relative to other areas of Watson Creek, possibly due to a buildup of fines on the creek bottom and surrounding marsh area. Sieve analysis of material from the water-table aquifer taken while drilling wells OF-30 and OF-31 shows that more than 50 percent is fine sand and silt.

A vertical hydraulic conductivity of 0.0045 ft/d was assigned to the upper confining unit in all appropriate areas of Gunpowder Neck and Watson Creek. For the Gunpowder River and Chesapeake Bay where the upper confining unit was not present, a value of 1,000 ft/d was

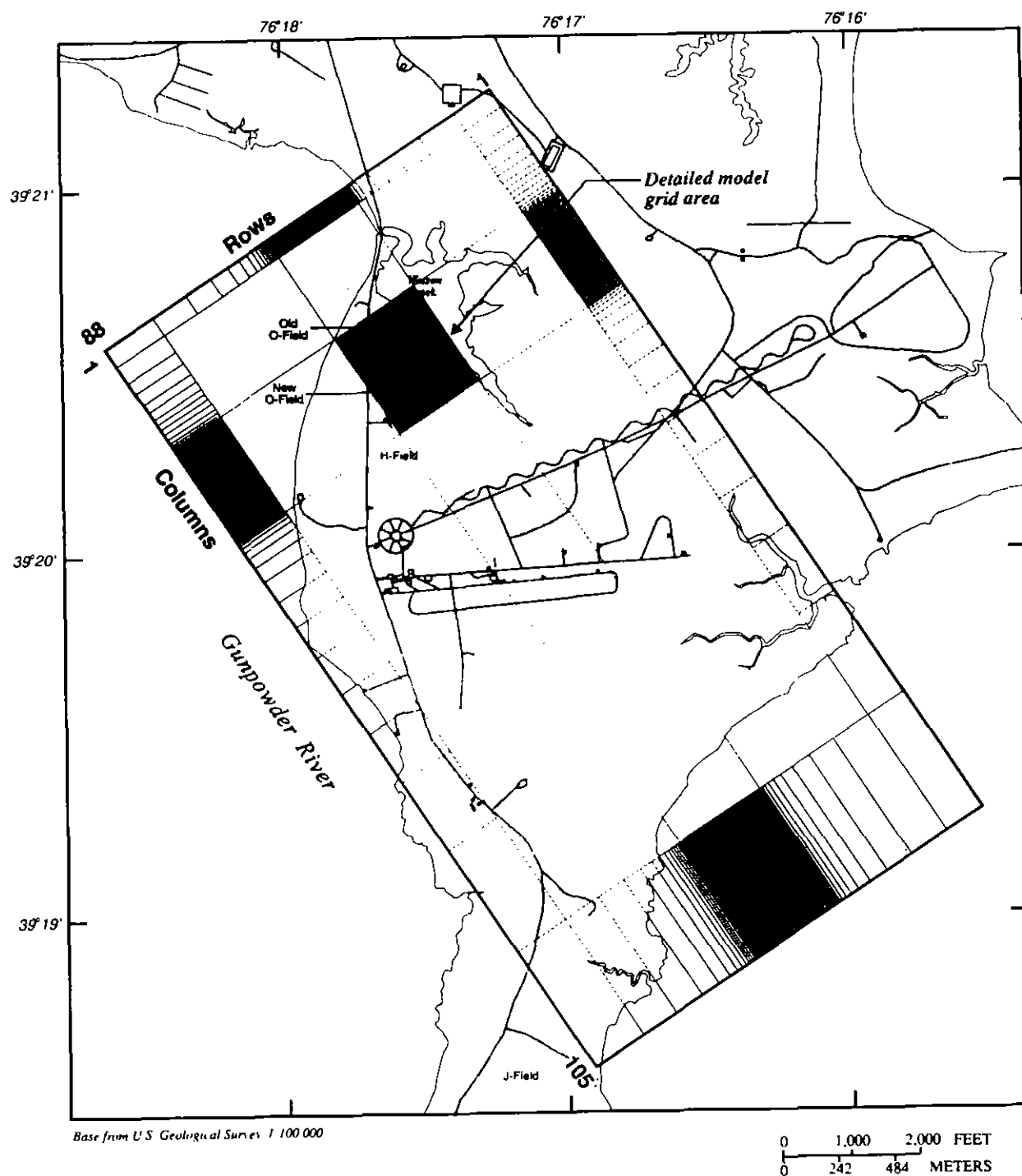
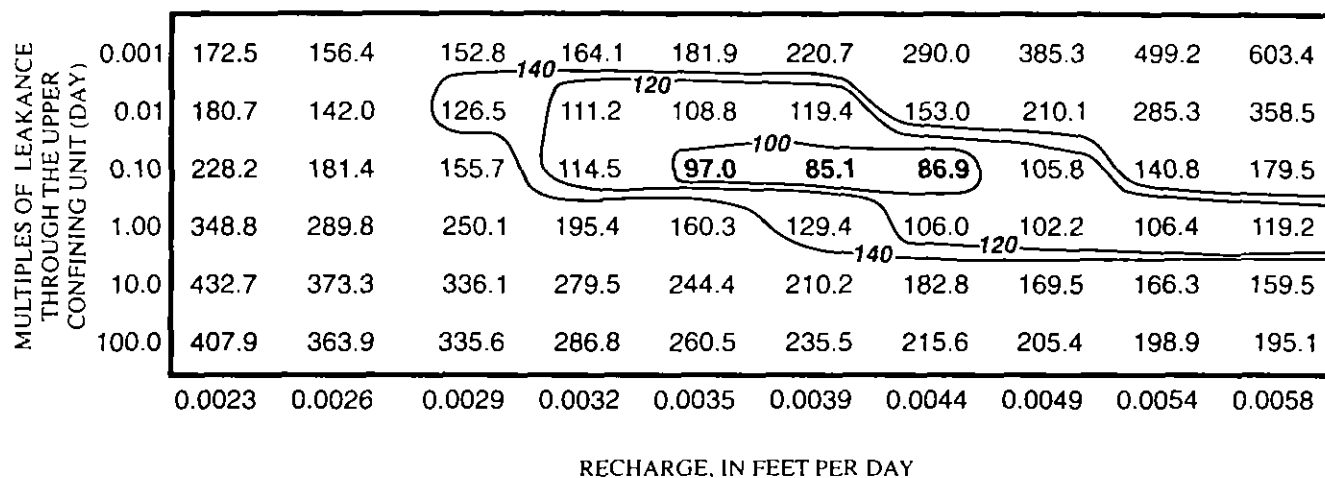
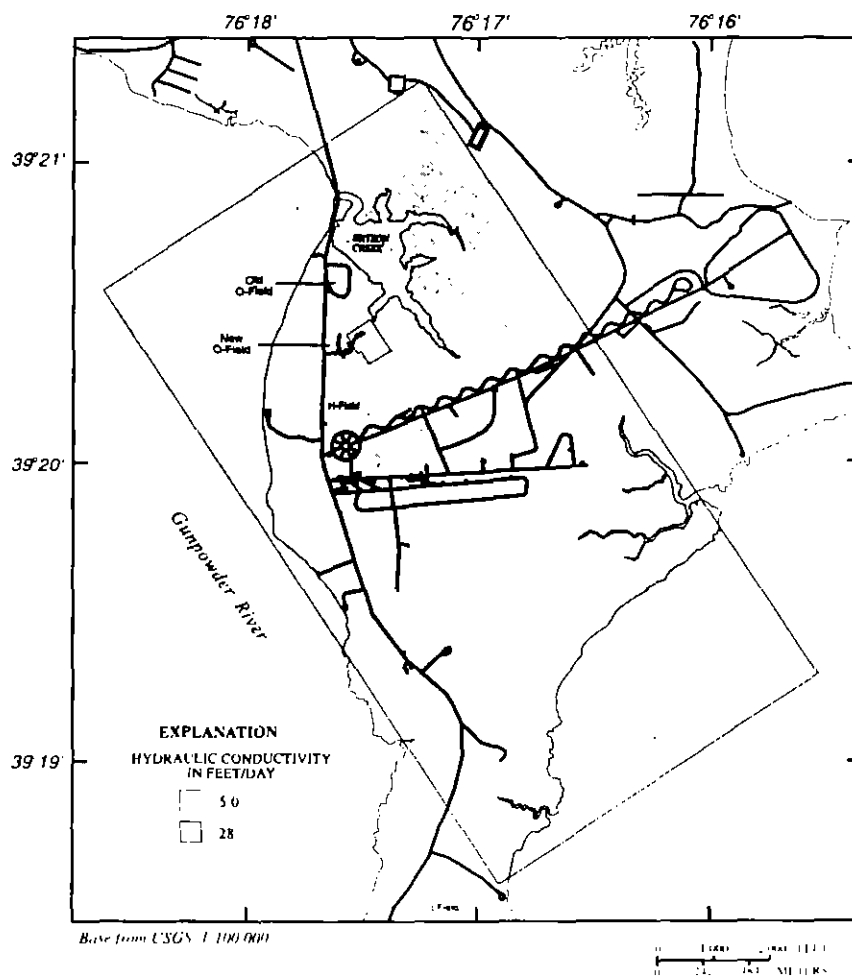


Figure 10. Finite-difference grid and model boundaries at O-Field.



**Figure 11.** Error between measured and simulated water levels with respect to multiples of leakance through the upper confining unit and recharge to the water-table aquifer.



**Figure 12.** Distribution of hydraulic conductivity in the water-table aquifer at New O-Field.

assigned to ensure that vertical movement of ground water was not restricted. The vertical hydraulic conductivity of the upper confining unit was divided by its thickness so that leakance changed areally in the model (fig. 13). Transmissivities of the upper confined aquifer used in the current model were modified from those used in the previous model by Vroblesky and others (1989). A transmissivity value of 283 ft<sup>2</sup>/d was used for cells beneath the Gunpowder Neck peninsula and Watson Creek. A value of 600 ft<sup>2</sup>/d was used for cells beneath the Gunpowder River and Chesapeake Bay, where the sediments are probably more permeable.

The model was calibrated by changing the values of poorly known variables through reasonable ranges while holding measured or

calculated variables constant. The transmissivity of the upper confined aquifer and the hydraulic conductivity of the water-table aquifer were well defined from the previous flow models and aquifer tests. However, no measured data were available on the recharge rate to the water table and very little data were available on the vertical hydraulic conductivity of the upper confining unit.

Recharge rates and the vertical hydraulic conductivity of the upper confining unit were changed through ranges of reasonable values and the sum of the squared errors for each change was calculated. A matrix was plotted to compare the results and the local minima of errors with respect to the recharge rate and the vertical leakance values (fig. 11). A recharge rate of 0.0039 ft/d or 17 in/yr, coupled with a vertical hydraulic conductivity

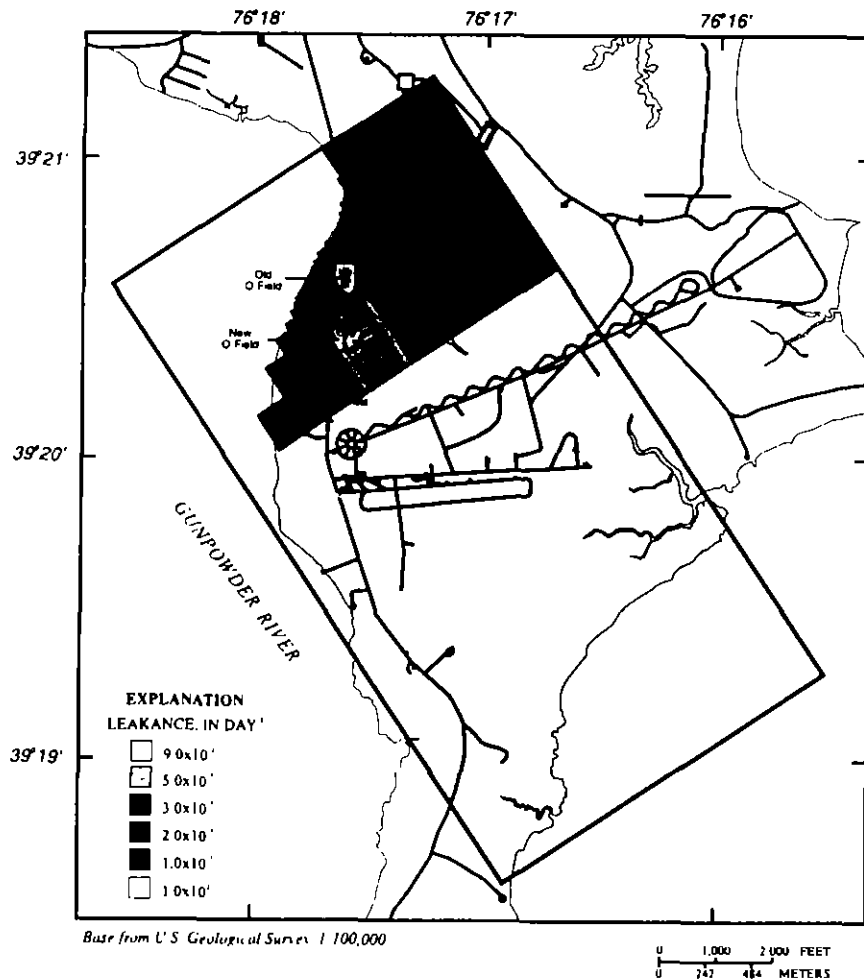


Figure 13. Distribution of leakance in the upper confining unit at New O-Field.



0.01 times the original, or 0.00045 ft/d for the peninsula and Watson Creek, and 10 ft/d for the bay and river produced the lowest sum of squared errors for both layers, which was 85.1 ft.

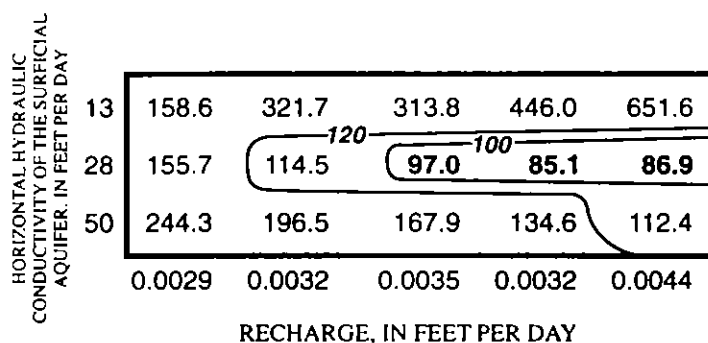
#### **Sensitivity Analysis**

After calibrating the current model by establishing the local minima with respect to the two least known variables (recharge to the water-table aquifer and leakance through the upper confining unit), the hydraulic conductivity of the water-table aquifer was tested to indicate the sensitivity of the model to changes in that parameter. Because both slug and pump tests have been performed on various wells around O-Field, hydraulic conductivity values were changed to reflect reasonable maximum and minimum values based on these data. Hydraulic conductivity values in the current calibrated model were changed based on the exclusion of censored (less than 0.1 ft/d) slug test data from Vroblesky and others (1989). Vroblesky and others (1989) indicated that a number of wells on which slug tests were performed did not respond to the introduction of the slug because fine sediment clogged the well screen. By excluding hydraulic conductivity data from these wells, the median horizontal hydraulic conductivity in the current model was increased to 50 ft/d. A series of model runs was then executed in which values for leakance and a horizontal hydraulic conductivity value of 50 ft/d were used while varying selected recharge rates as described above (fig. 11). Vroblesky and others (1989) stated that in wells where a hydraulic conductivity below a censoring threshold of less than 0.1 ft/d was measured, the actual hydraulic conductivity was probably between 4 and 30 ft/d. Excluding all but the censored slug test data and assuming a median value for horizontal hydraulic conductivity of 13 ft/d for the values less than 0.1 ft/d provided a reasonable value for a minimum horizontal hydraulic conductivity. The current model was then run varying selected recharge values against leakance and with a horizontal hydraulic conductivity of 13 ft/d.

A matrix of the sum of squared errors, for both layers, for each of the sensitivity tests for the three values of horizontal hydraulic conductivity show that a local minima with respect to recharge (and leakance) had been established (fig. 14) using a horizontal hydraulic conductivity of 28 ft/d. This solution, however, does not represent a unique combination of model parameters. There were indications at the peripheries of the matrices that changes, beyond those tested, could possibly produce another local minima. No other local minima found in the matrices, however, were as low in error as that established previously.

#### **Implication of Chlorofluorocarbon Data**

Of the six wells sampled for CFC's, wells OF-23 and OF-37 were contaminated with CFC-11 and CFC-12. Although wells OF-39 and OF-10 probably are not contaminated, data from those wells were not used for several reasons. The annular seal on well OF-10 appeared to be faulty, potentially providing contact between the sampled aquifer material and modern (1993) air. The screen length of well OF-39 made it doubtful that water sampled from the well would be exclusively from the water-table aquifer. The location of well OF-39 in the flow system allowed for the potential of flow to the southeast, away from well OF-10, the nearest site downgradient from well OF-39. The remaining two uncontaminated wells, OF-3 and OF-9, defined a line approximately parallel to ground-water flow. Well OF-3 (fig. 4) is located near the topographic high of the study area and contains ground water with a modeled age of 14.3 years (table 1). Well OF-9 is located 1,274 ft to the northwest, and downgradient of well OF-3. Water from well OF-9 had a CFC modeled age of 23.3 years, implying that water recharged near well OF-3 takes 9 years to travel to well OF-9, at an average velocity of 0.39 ft/d. Equation 1 was solved for  $K$  so that CFC data could be related to the modeled parameter of horizontal hydraulic conductivity. This resulted in a horizontal hydraulic conductivity of 26 ft/d--an estimate independent of the model or the aquifer-test data. The data from the measured heads of June 1993



**Figure 14.** Error between measured and simulated water levels with respect to the horizontal hydraulic conductivity of the water-table aquifer and selected recharge values to the water-table aquifer. The values inside of the 100 contour indicate the range of solutions with the lowest error.

(target heads used to calibrate the steady-state model) were used to compute a slope from well OF-3 to well OF-9 (table 2). Using a porosity of 0.4 and a horizontal hydraulic conductivity of 28 ft/d, an average velocity of 0.42 ft/d was computed from well OF-3 to well OF-9. This represents a traveltime between these wells of 8.3 years.

Initially, when modeled heads were substituted for measured heads, average velocities increased to 0.63 ft/d, which is equivalent to a traveltime between well OF-3 and well OF-9 of 5.5 years. The increase in velocity using calculated heads from the flow model was the result of a 3.91-ft increase in the head at well OF-3 and a 1.1-ft decrease in head at well OF-9 between the modeled versus measured heads. This increased the slope of the water table between the two wells by 40 percent. Errors such as these could be the result of inaccurate representation of one or several modeled parameters or errors in CFC data collection or analysis. In their model, Vroblesky and others (1989) suggest that the upper confining unit becomes more permeable and thins to the south--implying that water could pass more easily

between the water-table and upper confined aquifers. By altering the current calibrated model so that the leakance of the upper confining unit is 0.09 d<sup>-1</sup> for all cells immediately southeast of New O-Field, calculated heads in well OF-3 were effectively reduced to within about 2 ft below the measured head, while heads for well OF-9 were raised to less than 1 ft below the measured head. This change reduced the slope to within about 12 percent of the slope computed using measured heads, thereby decreasing the average velocity of ground water between the two wells to 0.48 ft/d, which is equivalent to a traveltime between well OF-3 and well OF-9 of 7.4 years. When the values for CFC (9.0 years) and modeled (7.4 years) traveltime are compared to the velocity derived from measured heads (8.3 years), there is less than 12 percent difference. This comparison illustrates (1) that the current model simulates the slope of the water table in the area of well OF-3 and well OF-9 with reasonable accuracy when compared to the measured values of June 1993, and (2) horizontal hydraulic conductivity values generated from aquifer tests are corroborated by CFC data when measured heads are used in conjunction with an assumed porosity of 0.4.

**Table 2.** *Traveltime of ground water between wells OF-3 and OF-9 at New O-Field, based on chlorofluorocarbon data, hydraulic heads measured in June 1993, and modeled hydraulic heads*

[ft = feet; ft/d = feet per day]

	Hydraulic head (ft)		Change in head ( $\Delta h$ ) (ft)	Hydraulic conductivity (ft/d)	Velocity (ft/d)	Travel-time, (years)
	Well OF-3	Well OF-9				
CFC data	6.36	14.00	7.64	26	0.39	9.0
Measured	6.36	14.00	7.64	*28	.42	8.3
Modeled	4.33	13.01	8.68	*28	.48	7.4

\* Value used in model.

The use of shallow ground-water age-dating techniques demonstrates that CFC data can be used effectively as a tool to refine the knowledge of the physical properties governing ground-water flow. The changes to the calibrated flow model described above provided a more representative simulation of the water-table aquifer. The CFC-modeled age data, in conjunction with a knowledge of the geology of the area, provide independent insight to the properties governing the hydrologic system.

## Flow Paths

Ground-water flow paths and heads in the calibrated model closely follow those interpreted from measured hydraulic heads in June 1993 (fig. 15). Seasonal changes in water levels could change the directions of ground-water flow. Changes in water levels, however, are centered about an average annual water level, which is what the calibrated model represents. Because ground-water flow is slow compared to seasonal changes in water levels, temporary changes in velocity tend to be negligible over long periods of time and an average flow rate is valid.

From the chlorofluorocarbon-modeled age dates, a rate of ground-water flow of 0.39 ft/d was estimated between wells OF-3 and well OF-9 south of New O-Field. An estimate of the velocity of ground water based on the ground-water-flow model of 0.48 ft/d was calculated for the same path based on the hydraulic gradients of the flow model and the equation for the average linear velocity (Lohman, 1979). An effective porosity of 40 percent was assumed for the water-table aquifer in the calculation. The velocities estimated from independent (CFC) data indicate that the rates of ground-water flow south of the O-Field area can be estimated by the ground-water-flow model with reasonable accuracy.

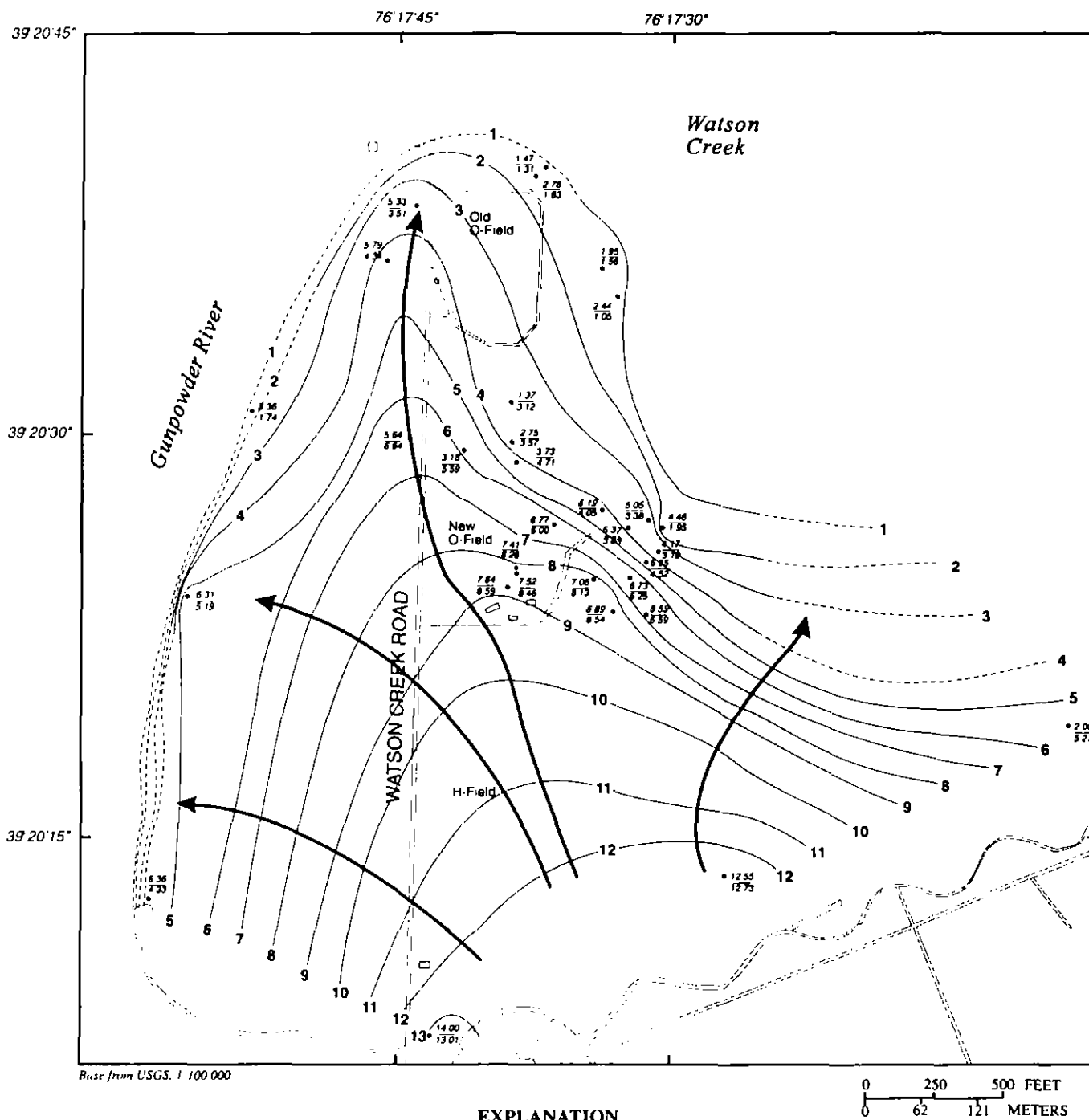


Figure 15. Measured and simulated hydraulic heads of the water-table aquifer at O-Field, June 1993.

## SUMMARY

The U.S. Army disposed chemical agents, contaminated materials, and unexploded ordnance at O-Field in the Edgewood Area of Aberdeen Proving Ground, Maryland. Soil, ground water, surface water, and wetland sediments in the O-Field area were contaminated from the disposal activity. The USGS began a study in cooperation with the U.S. Army in 1990 to (1) further define the hydrogeologic framework of the O-Field area, (2) characterize the hydraulic properties of the aquifers and confining units, and (3) define ground-water flow paths at O-Field based on the new data and new simulations of ground-water flow.

The water-table aquifer, the upper confining unit, and the upper confined aquifer comprise the shallow aquifer system of the O-Field area. The lower confining unit is considered a lower boundary to the shallow aquifer system through which ground-water movement is negligible. These units are within the Talbot Formation of Pleistocene age or more recently reworked alluvium of the Holocene.

A previous USGS ground-water-flow model of the O-Field area was redesigned with new data and with emphasis on New O-Field. The current model was calibrated to water levels of June 1993. The model was calibrated by changing the values of the least known variables through reasonable ranges while holding measured variables constant. Ground-water flow paths in the calibrated model follow closely those interpreted from hydraulic heads measured in June 1993.

On the basis of chlorofluorocarbon dates, a rate of ground-water flow of 0.39 ft/d was estimated between two wells south of New O-Field. These data were used to change the calibrated ground-water-flow model so that modeled heads in the water-table aquifer more closely reflected the velocity implied by the CFC data. The refined model produced an estimate of ground-water velocity of 0.48 ft/d for the same flow path based on the hydraulic gradients from the flow model and the equation for the average linear velocity.

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